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# A kinetic study of hydroxyl radical-catalyzed decomposition of chloroform

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# A KINETIC STUDY OF HYDROXYL RADICAL-CATALYZED DECOMPOSITION OF CHLOROFORM

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By

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ABSTRACT

A KINETIC STUDY OF HYDROXYL RADICAL CATALYZED DECOMPOSITION OF CHLOROFORM

By C. Travis Rappleye

Chloroform, a known carcinogen, is introduced into drinking water as a result of the chlorination process. Chloroform removal can be achieved through the use of chemical degradation by hydroxyl radicals produced through the photolysis of hydrogen peroxide. Sodium percarbonate, a solid source of hydrogen peroxide in solution, is attractive because it is easier to handle than liquid hydrogen peroxide. Sodium percarbonate produces a solution with a high pH, and high pH has been shown to limit the efficacy of chloroform decomposition by hydroxyl radicals. In this study, the effect of pH on the kinetics of decomposition of chloroform by hydroxyl radicals was examined, with the intent to determine whether sodium percarbonate could be used as a solid source of hydrogen peroxide. Within the experimental parameters studied, no dependence of rate constant on chloroform concentration or pH was found, but a dependence of rate constant on hydrogen peroxide concentration at pH 12 was found.

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To my mom, Margie, for always believing in me and always giving me encouragement. To my dad, Earl, for giving me a fresh start in life so that I could even go to school and reach this great accomplishment.

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# CHAPTER 1. INTRODUCTION

Chlorinated hydrocarbons pose health risks, such as toxicity, carcinogenicity, and teratogenicity when ingested through drinking water.[1] Before it is piped to the customer, drinking water is stored in large, open reservoirs that are home to wildlife such as birds, fish, plants, and even bacteria. Some of the bacteria, such as Esheria coli,[2] is harmful to humans and must be removed before the water is considered potable. Several methods are available to control the bacteria in drinking water, which include chlorination, ozonation, and chloramination.[1] In all three cases, reagents are added to the water to control bacteria levels. In the case of chlorination, chlorine is simply added to water to kill bacteria. In ozonation and chloramination, the reagents are formed *in-situ* from reagents added to the water.

While ridding the water of bacteria, microbial control of the water by chlorine, chloramine, and chlorine dioxide leave behind potentially harmful products of the decomposition. Each chemical leaves behind a unique set of byproducts, as seen in Tables 1 and 2.

**Table 1. Byproducts formed by chlorination[1]**
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| Oxidation byproducts | Concentrations,[b] µg/liter | | Reference |
|---|---|---|---|
| | Median | Maximum | |
| THMs | | | |
| Chloroform | 25 | 240 | ILSI (*25*) |
| Bromodichloromethane | 9.5 | 90 | ILSI (*25*) |
| Chlorodibromomethane | 1.6 | 36 | ILSI (*25*) |
| Bromoform | <0.2 | 7.1 | ILSI (*25*) |
| HAAs | | | |
| Dichloroacetic acid | 15 | 74 | ILSI (*25*) |
| Trichloroacetic acid | 11 | 85 | ILSI (*25*) |
| Bromochloroacetic acid | 3.2 | 49 | ILSI (*25*) |
| Monochloroacetic acid | 1.3 | 5.8 | ILSI (*25*) |
| Dibromoacetic acid | <0.5 | 7.4 | ILSI (*25*) |
| Monobromoacetic acid | <0.5 | 1.7 | ILSI (*25*) |
| Tribromoacetic acid | — | — | — |
| Bromodichloroacetic acid | — | — | — |
| Chlorodibromoacetic acid | — | — | — |
| HANs | | | |
| Dichloroacetonitrile | 2.1 | 10 | ILSI (*25*) |
| Bromoacetonitrile | 0.7 | 4.6 | ILSI (*25*) |
| Bromochloroacetonitrile | 0.6 | 1.1 | Cumming and Jolley (*59*) |
| Dibromoacetonitrile | <0.5 | 9.4 | Cumming and Jolley (*59*) |
| Trichloroacetonitrile | <0.02 | 0.02 | Cumming and Jolley (*59*) |
| Tribromoacetonitrile | — | — | — |
| Haloketones | | | |
| 1,1,1-Trichloropropanone | 1.0 | 8.3 | ILSI (*25*) |
| 1,1-Dichloropropanone | 0.4 | 2.5 | ILSI (*25*) |
| 1,3-Dichloropropanone | — | — | — |
| Others | | | |
| Chlorate | 161 | 9180 | ILSI (*25*) |
| Chloral hydrate | 2.1 | 25 | ILSI (*25*) |
| Chloropicrin | 0.4 | 3.7 | ILSI (*25*) |
| MX | 0.005 | 0.067 | Bull (*7*) |
| Cyanogen chloride | 0.62 | — | Cumming and Jolley (*59*) |
| Cyanogen bromide | — | — | — |
| Halonitriles | 0.4 | 3.7 | Richardson (*49*) |

Abbreviations: HAAs, haloacetic acids; HANs, haloacetonitriles; ILSI, International Life Sciences Institute; MX, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone. [a]Studies have primarily focused on surface water systems where high DBPs would be expected. [b]Median and maximum concentrations vary widely depending on the chemical/time/source of sampling.

**Table 2. Byproducts from ozonation, chlorine dioxide, and chloramination.[1] Reprinted with permission from *Environmental Health Perspectives*.**

| Oxidation byproducts | Range of concentrations, µg/liter | Reference |
|---|---|---|
| Principal products formed by use of ozonation | | |
| Aldehydes | | |
| Formaldehyde | 1–50 | Reckhow and Singer (*94*) |
| Acetaldehyde | 1–50 | Reckhow and Singer (*94*) |
| Glyoxal | ND–15 | Ferguson et al. (*95*) |
| Dimethyl glyoxal | 0.005–3 | Richardson (*49*) |
| Methyl glyoxal | ND–8 | Richardson (*49*) |
| Benzaldehyde | 0.005–3 | Richardson (*49*) |
| Brominated byproducts | | |
| Bromate | 1–50 | Reckhow and Singer (*94*) |
| Bromoform | 1–50 | Reckhow and Singer (*94*) |
| Brominated acetic acids | 1–50 | Reckhow and Singer (*94*) |
| Bromopicrin | 1–50 | Reckhow and Singer (*94*) |
| Principal products formed by use of chlorine dioxide | | |
| Chlorite | 0.01–5.36 | U.S. EPA (*96*) |
| Chlorate | 0.01–4.42 | U.S. EPA (*96*) |
| Plus similar oxidation byproducts as ozonation | — | — |
| Principal products formed by chloramination | | |
| Similar to chlorination but lower THMs, lower cyanogen bromide | — | — |
| Enhanced levels of cyanogen chloride | — | — |
| Enhanced levels of larger hydrophilic organic halides not further defined | — | — |

ND, not detectable.

These halogenated decomposition byproducts (DBPs) can pose health risks of their own, as shown above, and each must be evaluated. Among the three chlorine-based methods for microbial control, chlorination is the most common because it has a long history of use and is easier to use than other methods.[2] As mentioned above, chlorination requires the addition of one reagent but ozonation and chloramination require formation *in-situ* from more than one reagent. With this method, the most prevalent and therefore the most widely studied decomposition byproduct is chloroform, as it is the most abundant decomposition product.[3]

In 1992, in response to the growing concern over the toxicity of chloroform and other DBPs, the EPA began the process of putting regulations in place to limit the

concentrations of DBPs in drinking water. At that time, there was not enough data on toxicity, cost, removal technology, etc. to impose a comprehensive set of regulations.

Recognizing the immediacy of the problem, the EPA chose to impose a two phase regulation process. The first phase, Stage 1, would serve to set limits on DBPs with limited information with the intent of preventing levels from rising. Stage 2, finalized in 2002, imposed limits on levels of chloroform in drinking water based on toxicological data. These limits require water handling agencies to monitor chloroform levels in drinking water. When chloroform levels exceed the limits set by EPA, water handling agencies must bring the levels within these limits.

Several methods are available for the removal of chloroform from drinking water and all are potential candidates for industrial use. The methods available can be placed into two categories: filtration or decomposition *in-situ*. The filtration system is an attractive option as it can be easily understood by water plant workers and integrated into existing water cleaning processes at reservoirs. The major downside to filtration is that the target compounds are not destroyed but merely transferred to another medium.[4] Industrial filtration involves cartridges or elements that are used and then regenerated. One important risk is that the filter cartridges will be discarded improperly and the filtered compounds will become re-introduced into the water table.

Because of the risks associated with using filtration to clean drinking water, *in-situ* decomposition methods can be an attractive alternative removal method.[1, 3, 5] All of the methods developed to date involve the use of radicals to decompose organics. Decomposition has the major benefit that the potential exists for the reactants to be

chosen such that the products are benign. The potential also exists for the system to be made cheaper than filter cartridges.

There are two major types of *in-situ* decomposition: catalytic and non-catalytic decomposition.[5] As stated earlier, both methods generate radicals that then decompose the target compounds. Catalytic methods use soluble transition metal compounds to catalyze the formation of radicals from suitable precursors, which then in turn attack the compounds of interest.[6-8] Non-catalytic methods generate the radicals by dissociation of a meta-stable compound.[5, 9-11]

Catalytic methods typically use transition metal compounds to mediate the formation of radicals from radical precursors.[6] So far, the systems developed are $TiO_2/H_2O_2$,[7] $RuO_4/H_2O_2$,[6] and $Pd/H_2$.[8] The benefit is that the catalyst is renewed in a reaction and therefore can be used many times. Depending on the reaction rate, a catalyst can be used in very low concentrations if it is renewed quickly. One of the serious drawbacks to using a catalyst system is the risk of contamination of the drinking water by the catalyst itself.

Another consideration with the catalytic systems listed above is that they all operate by dissociating a reactant, in these examples hydrogen peroxide or hydrogen, that is not normally present in water and therefore must be added. This obviously makes these systems less renewable than if the decomposition agent were just the catalyst. All of these methods have a crucial component that must be continually added, in these cases either hydrogen peroxide or hydrogen. No catalyst has been developed that will effectively generate radicals from compounds already present in the water.

Non-catalytic methods also require the continual addition of a reactive component. The positive aspect is that there is no transition metal component to worry about. Non-catalytic systems include $H_2O_2/O_3$,[5] $H_2O_2/UV$,[11] $O_3/UV$,[9] and high pH.[10] Besides the absence of transition metal compounds, the above reactions include only "clean" compounds that decompose into water and oxygen. This means that any excess reactant will safely decompose and not require safeguards to protect from or remove reactants.

Of the non-catalytic methods, the $H_2O_2/UV$ system is the most attractive.[3] Not only is it "clean," but the other three methods use ozone, which is a gas and more difficult to use because of low solubility in water. Ozone, being poisonous, colorless, and odorless, can also pose a health hazard to plant workers if allowed to build up in work areas. The threshold limit value (TLV) for exposure is 0.20 ppm for less than 2 hours.[12]

Storage and handling of liquid concentrated hydrogen peroxide can be dangerous as well. The release of oxygen in an enclosed container can cause pressure to build up. Concentrated liquid hydrogen peroxide causes chemical burns to skin and serious damage to eyes.[13] It would be convenient to find a more stable and safe to handle form of hydrogen peroxide. One possibility is sodium percarbonate, which is a solid form of hydrogen peroxide, and is more stable and safer to handle.

The chemical formula sodium percarbonate is $[Na_2CO_3]_2 \cdot 3H_2O_2$ and upon dissolution in water, this compound dissociates into sodium carbonate and hydrogen peroxide.[14] Sodium percarbonate is found in many household oxygen cleaners, such as OxiClean, Oxy-Boost, and others. The household versions contain about 25% sodium percarbonate and about 75% sodium carbonate. The sodium carbonate serves to stabilize

the sodium percarbonate and extend the shelflife.[15] Commercially pure sodium percarbonate can be purchased from fine chemical manufacturers.

It would be convenient for adopters of the $H_2O_2$/UV system to use sodium percarbonate as a hydrogen peroxide source. It is a solid, not light sensitive, and has a relatively long shelflife.[16] Ease of storage is not the only consideration; sodium percarbonate does not cause chemical burns when it comes into contact with skin,[17] as does liquid hydrogen peroxide.

One major consideration with sodium percarbonate is that sodium carbonate solution has a pH of about 12 and is therefore very basic. Questions arise about how the chemistry of the system is affected as it is suspected that the chloroform decomposition by ·OH radicals is affected by pH. Rudra et al. suggested a competing reaction for hydrogen peroxide at high pH.[11]

$$H_2O_2 + OH^- \rightarrow \cdot OOH + H_2O \qquad (1)$$

At high pH, a reaction between hydrogen peroxide and the hydroxide ion dominates and consumes hydrogen peroxide at a very fast rate leaving little available for chloroform decomposition. The author made no mention of the rate of this reaction as a function of pH.

The purpose of this work was to study the pH dependence on the kinetics of decomposition of chloroform by ·OH radicals, with the ultimate goal of assessing the suitability of sodium percarbonate as a source of hydrogen peroxide. Rate constants as a function of hydrogen peroxide concentration, chloroform concentration, and pH were studied in order to better understand the factors that might affect the reaction kinetics.

Based on work by prior researchers, a strong dependence of rate constant on pH is expected.

Before the kinetics could be studied, an analytical method to detect the concentration of chloroform in water was needed. Analytical methods exist, but the most commonly used for this type of work require specialized equipment, as mentioned in Section 2.4 below. A simple method that uses GCMS to measure the level of chloroform in water was developed and is explained below.

# CHAPTER 2. METHOD DEVELOPMENT

## 2.1 Introduction

Very simple qualitative tests were first performed to answer some fundamental questions about the chemistry. These tests, described in Section 2.2, were used to probe for generalizations about how this chemistry progressed at high pH, in the absence of UV light, and in the absence of hydrogen peroxide.

An important part of working with concentrated hydrogen peroxide is knowing the concentration as hydrogen peroxide constantly decomposes into oxygen and water. This decomposition can be mitigated by protection from UV light and heat, but since the reaction cannot be stopped completely, measurement of concentration is important. A titrimetic method, described below in Section 2.3, was used to track the concentration of hydrogen peroxide over the course of this study.

As mentioned earlier, an analytical method that is simple, precise, and uses common equipment was necessary for this testing. Two analytical methods were evaluated, gas chromatography (GC), and gas chromatography mass spectrometery (GC-MS) were all evaluated for suitability for this study. A discussion of each method and the advantages and disadvantages of each can be found below in Section 2.4.

Other considerations, such as sample preparation prior to analysis on the GCMS instrument as well as buffer selection for the pH study, are described in Sections 2.5 and 2.6.

Finally, a comprehensive experimental procedure that describes sample preparation and analysis is described in Section 2.7.

## 2.2 Initial Experiments

Initial experiments confirmed that chloroform is decomposed by hydroxyl radicals that are produced by photolysis of hydrogen peroxide with UV light. Two simple benchtop methods were employed to make this determination; column height and pH. In the column height method, 3 mL chloroform and 3 mL hydrogen peroxide solution were added to a quartz test tube. The tube was then shaken vigorously to accelerate saturation of chloroform in water, and allowed to settle and separate. After the initial shaking, the mixture was not stirred; mixing was controlled by diffusion.

When exposed to UV light, chloroform decomposition occurred at the interface between the two layers and the reaction progress was tracked by monitoring the height of the chloroform layer. As it is decomposed, the chloroform layer gets shorter. The column height was measured and recorded as a function of time to test which cases caused decomposition.

Monitoring pH of the aqueous layer was also found to be a useful method by which to observe the reaction, as pH of the aqueous layer was found to decrease as the reaction progressed. In one case, with 5 mL 26% hydrogen peroxide solution, 1 mL chloroform, and UV irradiation, the pH was found to drop from 6 to 3 over a seven day period, as shown in Table 3. This method works less well in buffer solutions, such as sodium percarbonate solutions, that are by definition resistant to change in pH. Results of these qualitative tests are indicated in Table 3.

**Table 3. Initial experiments. 1 mL chloroform and 5 mL water, 10% sodium percarbonate solution, or 26% hydrogen peroxide solution were placed in a quartz test tube and the mixture was tested by the method listed over a seven day period.**

| Test | Aqueous Solution | Method | Decomposition? |
|---|---|---|---|
| SPC/$CHCl_3$ UV | 10% SPC | Column Height | No |
| $H_2O_2$/$CHCl_3$ UV | 26% $H_2O_2$ | pH | Yes |
| $CHCl_3$ UV | Water | pH | No |
| $H_2O_2$/$CHCl_3$ Dark | 26% $H_2O_2$ | pH | No |

2.3 Hydrogen Peroxide Concentration

Knowing the concentration of hydrogen peroxide is important because in later experiments, the concentration is controlled in order to study the reaction kinetics as a function of hydrogen peroxide. Hydrogen peroxide concentration was determined by the common permanganate titration method.[18] Twenty five milliliters hydrogen peroxide solution is diluted to 250 mL with water in a volumetric flask. 25.0 mL of this solution is transferred to a 500 mL conical flask, and 200 mL water is added. Twenty milliliters 3.75 M sulfuric acid is added to the solution in the flask and stirred. The solution is titrated with 0.100 M potassium permanganate to a persistent light violet endpoint. The concentration of hydrogen peroxide can be calculated with equation 1.

$$\underset{\text{(Purple)}}{2MnO_4^- + 5H_2O_2 + 6H^+} \rightarrow \underset{\text{(Clear)}}{2Mn^{2+} + 5O_2 + 8H_2O} \qquad (2)$$

The concentration of hydrogen peroxide reagent used for this study was measured at 26.0% in the beginning, and degraded to 24.4% over the course of the 18 months that experiments were performed. The concentration was monitored throughout the study and the amount used in samples was varied accordingly in order to achieve accurate concentrations of hydrogen peroxide.

## 2.4 Analytical Method

The first step in studying the decomposition of chloroform in water by hydrogen peroxide is to develop an analytical method that is sensitive, accurate, and precise. In EPA Method 8260B,[19] "Volatile Organic Compounds by Gas Chromatography Mass Spectrometry," the EPA outlines a method to study chloroform concentration in water by an adsorption-desorption technique. In this technique, chloroform is separated from water by adsorption in a purge-and-trap device and then introduced into a gas chromatograph mass spectrometer (GCMS) by desorption. While this method is effective, not all laboratories have access to such specialized equipment. It would be convenient to develop a method that would allow chemists with standard equipment to study this reaction. One goal of this project is to develop a method that is easy to perform, gives accurate results, and allows for the determination of the concentration of chloroform in water within the parts per million range.

Two methods were evaluated: gas chromatography and GCMS. Gas chromatography was not chosen due to the inability to distinguish between analyte and extraction solvent. GCMS is a more selective method and, because of the detector design (discussed below), was found to be a suitable analytical method for this study.

### 2.4.1 Gas Chromatography

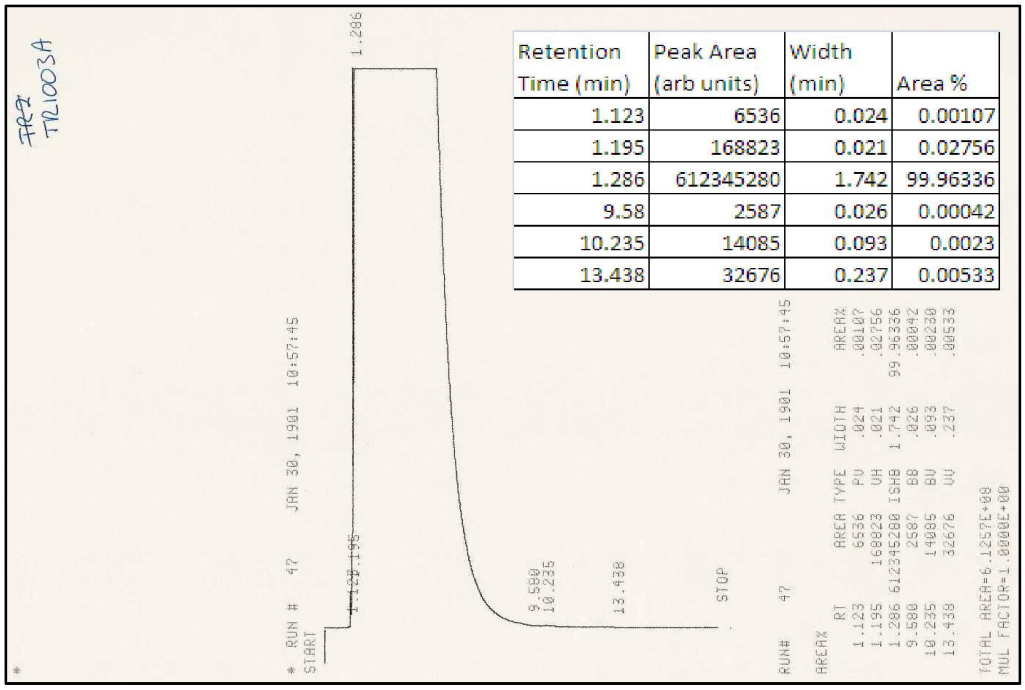
Gas chromatographs have become standard instruments in most chemistry laboratories and are used for many common analytical measurements. Gas chromatographs are inexpensive, reliable, and easy to use and maintain. To be amenable to analysis by gas chromatography, the analyte must meet several criteria. For gas chromatography, all compounds must be volatile and stable at the high temperatures

found in a gas chromatograph, typically 100 – 300 °C. If a compound is not volatile, for instance a high molecular weight polymer, it will either condense in the injection port as the solvent evaporates or decompose into smaller compounds due to the heat. Ions are excluded due to their nonvolatility, and they are also trapped in the inlet.

A gas chromatograph's inability to analyze ionic compounds does not preclude analysis of all solutions containing ions so long as the analyte itself is not ionic. A very common method used to separate non-ionic compounds of interest from a solution containing ions is liquid-liquid extraction. An ideal extraction solvent will dissolve the analyte, is immiscible with the original solvent, and is acceptable for introduction into a gas chromatograph. The extraction solvent is added to the solution, and the two are shaken to mix and then allowed to separate. When the two layers separate, a fraction of the compound of interest is dissolved in the nonpolar solvent according to its own polarity, but the ionic compound is not transferred to the extraction solvent. The extraction solvent can then be analyzed for concentration of analyte without interference from the ionic species.

Because only a fraction of the analyte may be partitioned into the nonpolar layer, the system must be calibrated in order to correlate concentration of analyte in extraction solvent to concentration of analyte in original solution. One major consideration with gas chromatography is that the solvent peak will almost certainly be much larger than the analyte peak, and the peaks must be well separated from each other. On a chromatogram, the area under a peak is proportional to its concentration in solution, so it is important to have well separated and well defined peaks.

In the first gas chromatography method attempted in this project, ether, which is more volatile than chloroform, was used as an extraction solvent. The thought was that the extraction solvent would elute before chloroform and leave a clean chloroform peak, but this was not the case. As can be seen in Figure 1, the chloroform and extraction solvent co-eluted (peak 3, 1.359 minutes).




| Retention Time (min) | Peak Area (arb units) | Width (min) | Area % |
|---|---|---|---|
| 1.123 | 6536 | 0.024 | 0.00107 |
| 1.195 | 168823 | 0.021 | 0.02756 |
| 1.286 | 612345280 | 1.742 | 99.96336 |
| 9.58 | 2587 | 0.026 | 0.00042 |
| 10.235 | 14085 | 0.093 | 0.0023 |
| 13.438 | 32676 | 0.237 | 0.00533 |

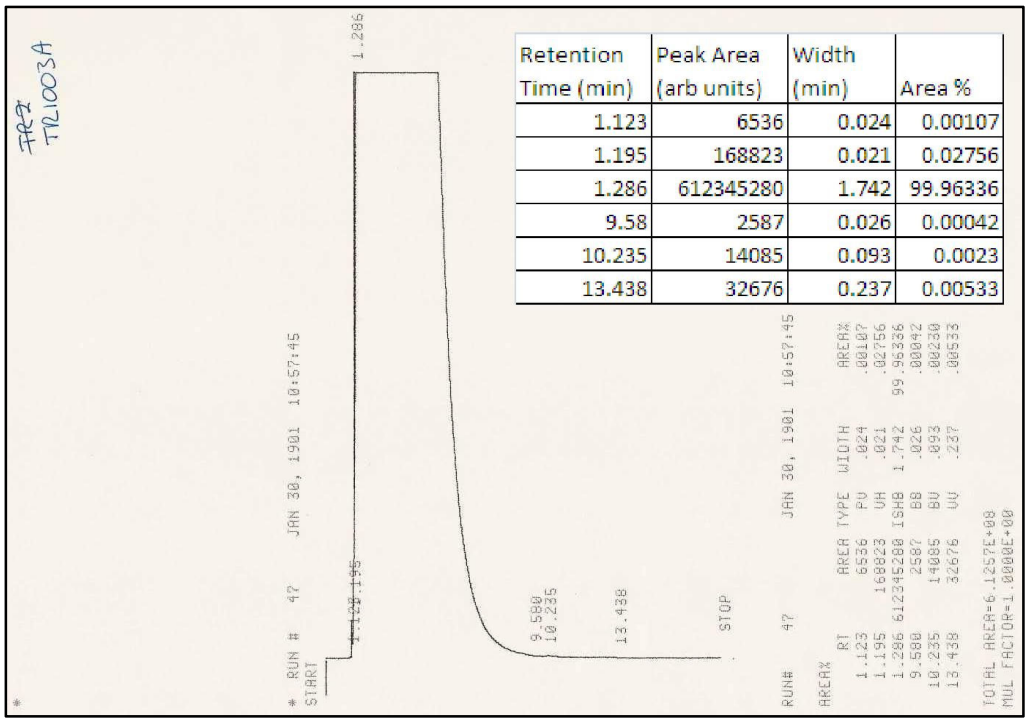
**Figure 1. Gas chromatogram of chloroform with ether extraction solvent. Chloroform extracted from saturated water solution (0.068 M chloroform) with 1 mL ether. The column used was 30 m x 0.25 mm, with 0.25 µm DB-5 stationary phase, 250 °C inlet temp, 100 °C oven temp, 2 mL/min helium.**

This is due to two factors; the compounds are both very volatile (see boiling points, Table 4) and therefore elute with the dead volume, and the concentration of extraction solvent is much greater than that of the chloroform. In this case, the peak for the extraction solvent is very wide and eclipses the solute peak.

**Table 4. Solvent and analyte boiling points**

| Compound | Boiling Point |
|---|---|
| Chloroform | 61.17 °C |
| Dichloromethane | 40 °C |
| Ether | 34.5 °C |
| Toluene | 110.63 °C |
| Dimethylpropane | 9.48 °C |

An attempt was then made to identify a solvent that would elute later than the analyte. Toluene, a less polar solvent with a higher molecular weight and higher boiling point, was chosen. As can be seen in Figure 2, the toluene co-eluted with the chloroform as well.

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| 9.58 | 2587 | 0.026 | 0.00042 |
| 10.235 | 14085 | 0.093 | 0.0023 |
| 13.438 | 32676 | 0.237 | 0.00533 |

**Figure 2. Gas chromatogram of chloroform with toluene extraction solvent. Chloroform extracted from saturated water solution (0.068 M chloroform) with 1 mL toluene (30 m x 0.25 mm column, 0.25 µm DB-5 stationary phase, FID detector, 250 °C inlet temp, 100 °C oven temp, 2 mL/min helium).**

Attempts to optimize separation were made by lowering the oven temperature and lowering the flow rate. In both instances, the elution time of the solvent and solute were slowed, but the peaks were not resolved. Even at 0.5 mL/min and 30 °C, the lowest practical settings for this analysis, the compounds still co-eluted.

Given that a reliable extraction solvent could not be identified, gas chromatography was abandoned as an analytical method. Another more selective analytical method, GCMS, was investigated.

2.4.2 GCMS

GCMS was then employed. GCMS instruments are typically less common in laboratories than GC or UV-VIS instruments but are becoming more widely available.

GCMS has the same limitation with respect to nonvolatile compounds and ions as traditional gas chromatography, but is much more sensitive and can be used to analyze compounds at very low concentrations (parts per thousand to parts per million range). Once an analyte has passed through the gas chromatography column, it is ionized and then introduced into a mass spectrometer, where it is characterized according to mass-to-charge ratio (m/z). This allows for the identification of individual components in the gas chromatogram by their mass spectra.

As with gas chromatography, an internal standard of known concentration is necessary due to the variability in injected sample size. For this system, the internal standard requires the following characteristics: no reaction with hydrogen peroxide, nonionic, volatile, similar boiling point to chloroform, and fast elution. No compounds that met all of the above criteria were identified. Many of the potential standards are organic and therefore susceptible to attack by hydroxyl radicals. A convenient way to circumvent this occurrence is to add an internal standard after the reaction has stopped (in this case, after removal from UV light), just before analysis. Reaction times in this study were 10 min, 20 min, 30 min, 60 min, 90 min, and 120 min. Since it has chemical characteristics similar to chloroform, including high volatility, dichloromethane was chosen as an internal standard.

Although GCMS can be used to de-convolute peaks that co-elute, it has a unique problem with respect to an extraction solvent. Because of the design of the detector (electron multiplier), large volumes of any eluent cause an overload. Typically, the extraction solvent must still be separated from the analytes, and the detector is actually turned off during the time that the solvent elutes from the column. Because no extraction

solvent was found to separate from the chloroform to a large enough extent, an alternative method for loading the sample was sought.

The volatility of chloroform and dichloromethane makes headspace measurements possible. Headspace samples take advantage of the volatility of analytes and are taken from the gas over a liquid sample. This sample can be injected directly onto a gas chromatography column without further preparation. Henry's law[20] states that for a dilute volatile compound in a liquid, the concentration, or partial pressure is proportional to its mole fraction, as shown in Equation 3.

$$P = k\chi \qquad (3)$$

Using this, the concentration of an analyte can be determined in the gas above a liquid and then the concentration in the liquid calculated. This method of sampling saves time and reduces the error involved inherent in extraction, namely pipetting error, while also leaving behind nonvolatile compounds. The solution is sealed into a vial with a septum and the gas above the solution is sampled.

The figures below illustrate how, with the preparation described above, a chromatogram can be acquired by GCMS, and transformed. Instead of a traditional detector that detects a constant analog input, the GCMS instrument works by taking mass spectra at intervals, typically hundreds of milliseconds apart, and then adding the spectra to produce a chromatogram. This is called a total ion current chromatogram and an example is shown in Figure 3.

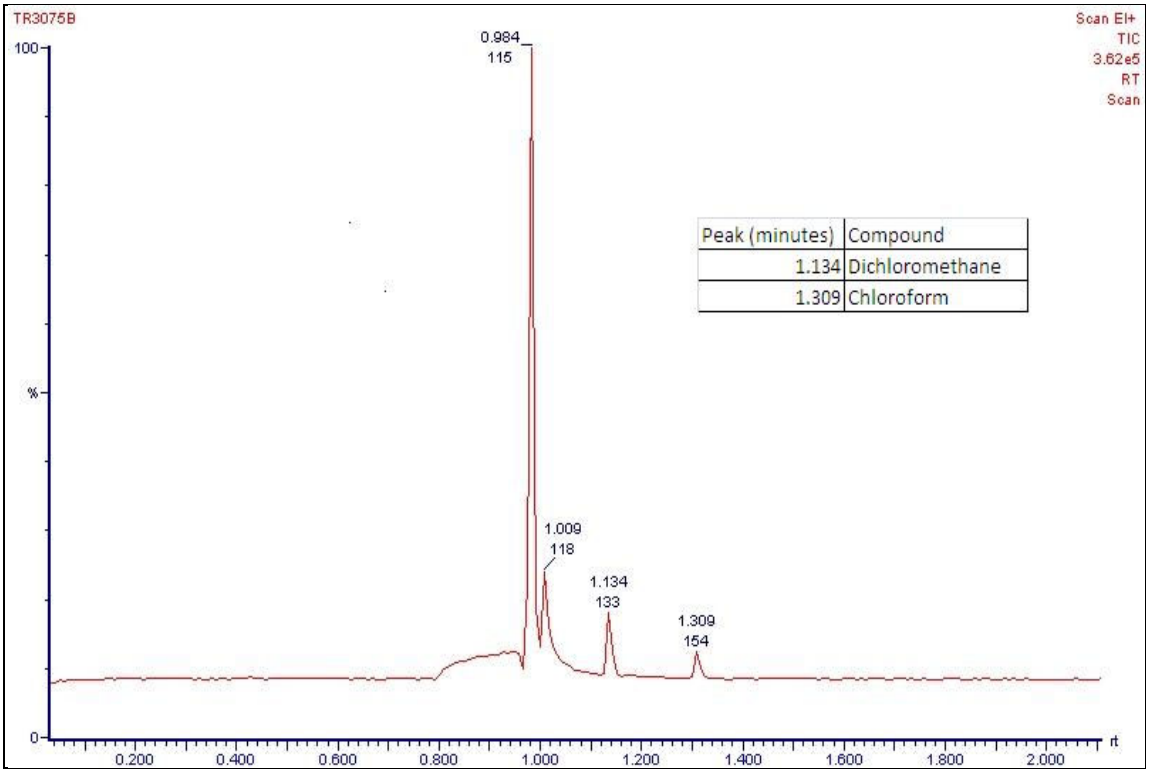


**Figure 3. Total ion current chromatogram of chloroform and dichloromethane in water. Conditions: 10 µL headspace sample taken from a pH 12 solution.**

A look at the mass spectrum in the center of the peak at 1.134 minutes (Figure 4) reveals that dichloromethane is present (denoted by *), but atmospheric species (denoted by **) such as water (m/z = 18), nitrogen (m/z = 28), and oxygen (m/z = 32) are also present, and in much higher quantities. The same is true for a chloroform peak at 1.309 minutes (Figure 5). Chloroform is denoted by +.

Once the sample has been run, a chromatogram can be constructed from the m/z ratios for the species of interest and all others excluded. The major m/z peaks for chloroform and dichloromethane are shown in Table 5.

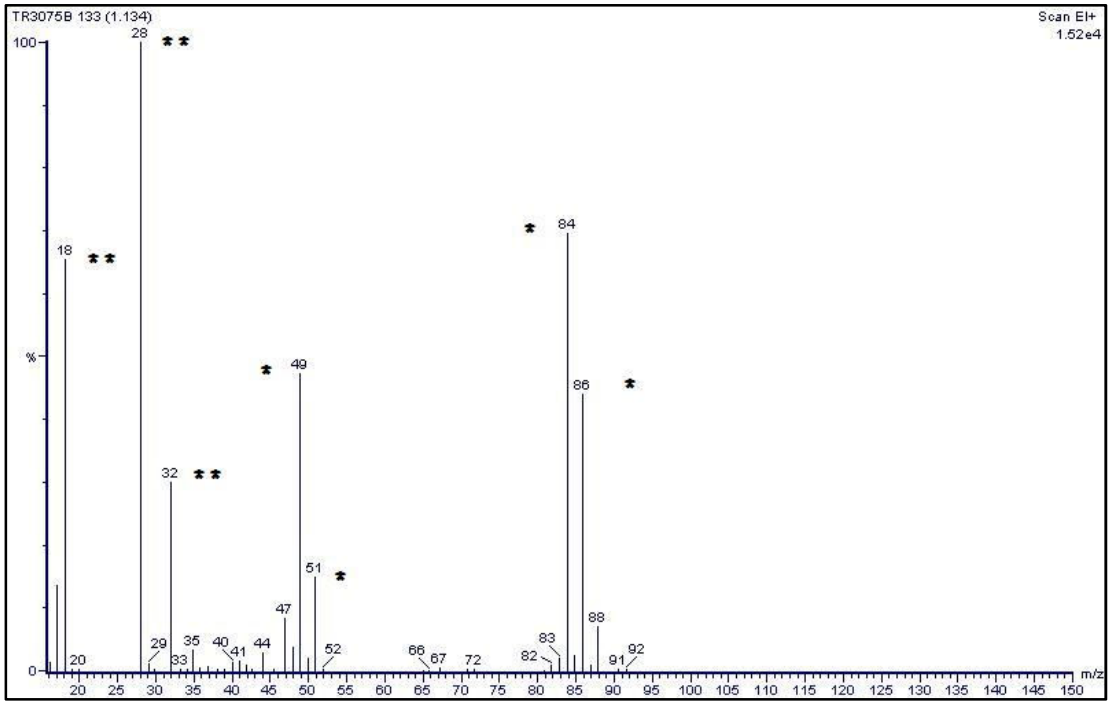


**Figure 4. Mass spectrum of dichloromethane peak.**

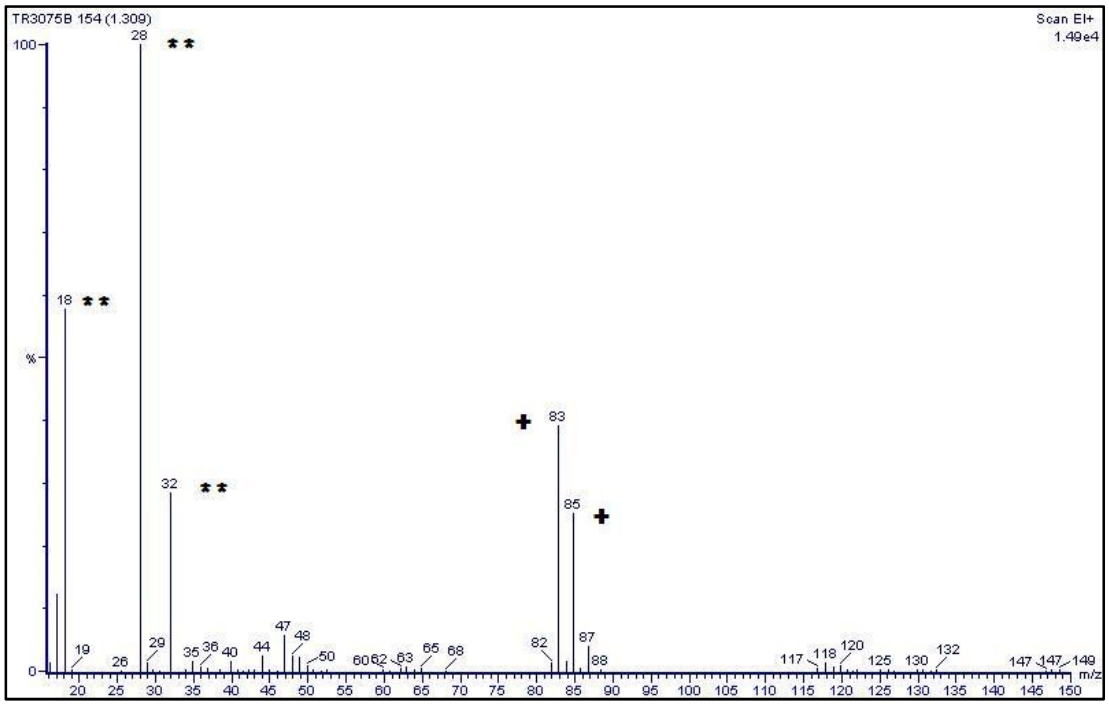


**Figure 5. Mass spectrum of chloroform peak.**

**Table 5. Mass spectrum peaks for chloroform and dichloromethane.**

| Compound | m/z Peaks |
|---|---|
| Chloroform | 83, 85 |
| Dichloromethane | 84, 86 |

Dichloromethane has major peaks at m/z 84 and 86. This is due to the removal of a hydrogen atom upon ionization and to the natural abundance of $Cl^{35}$ (75%) and $Cl^{37}$ (25%) isotopes. Chloroform has a higher molecular weight due to an additional chlorine atom, but as is apparent in Figure 5, is prone to fragmentation into smaller products upon ionization. Major peaks for chloroform are found at m/z 83 and 85. A chromatogram constructed from m/z peaks of 83, 85, and 86 is shown in Figure 6.

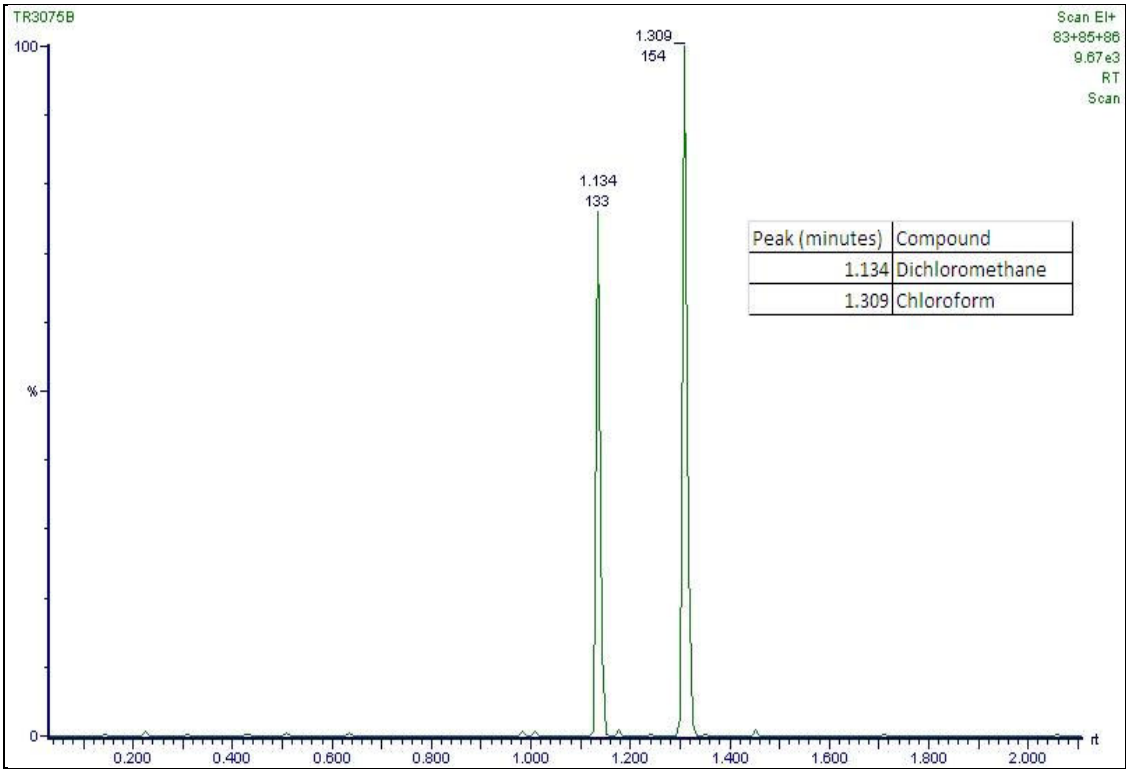


**Figure 6. Chromatogram based on m/z 83, 85, 86.**

The reason for including two major peaks from chloroform and only one from dichloromethane is that at the chosen concentration of dichloromethane standard, the peak at m/z 86 gave a sufficient peak area in the chromatogram. Since the concentration of chloroform varied during the course of an experiment, the peaks at m/z 83 and 85 were used in order to reduce the change in peak ratios over a wider range of concentrations of chloroform. Selecting peaks characteristic of the compounds of interest also greatly improves signal to noise ratio compared to straight gas chromatography. This system has

a linear dynamic range of at least 2 mM to 32 mM.

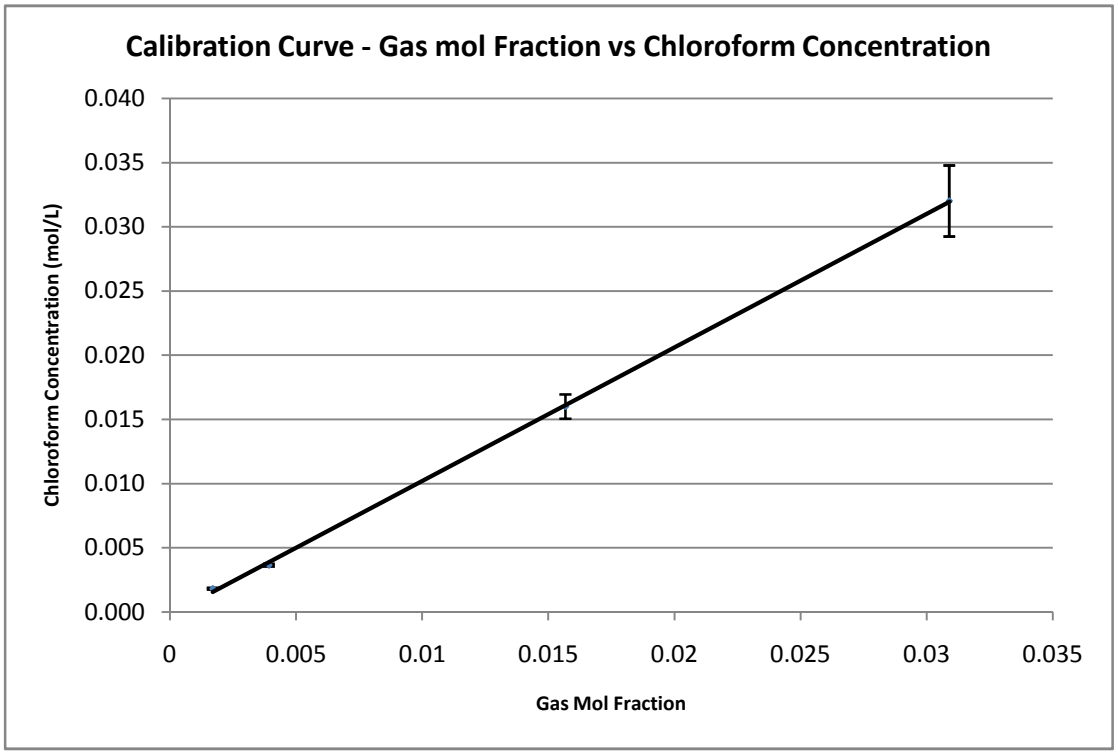


**Figure 7. Chloroform and dichloromethane calibration curve. Conditions: 10 µL headspace sample taken from samples with 0.002 M, 0.004 M, 0.016 M, and 0.32 M chloroform and 0.016 M dichloromethane in water.**

2.5 Sample Preparation

Once the dichloromethane is added and the vial capped with a septum, the gas phase must be allowed to come to equilibrium, which can take hours if left undisturbed because the diffusion controlled process is slow. This process can be accelerated by shaking the samples but there are inherent concerns about that method also. Immediately after the tube is shaken, tiny droplets of liquid are suspended in the gas. If a sample is taken during this time, these droplets can be aspirated into a needle and drastically affect the results, as shown below in Figure 8.

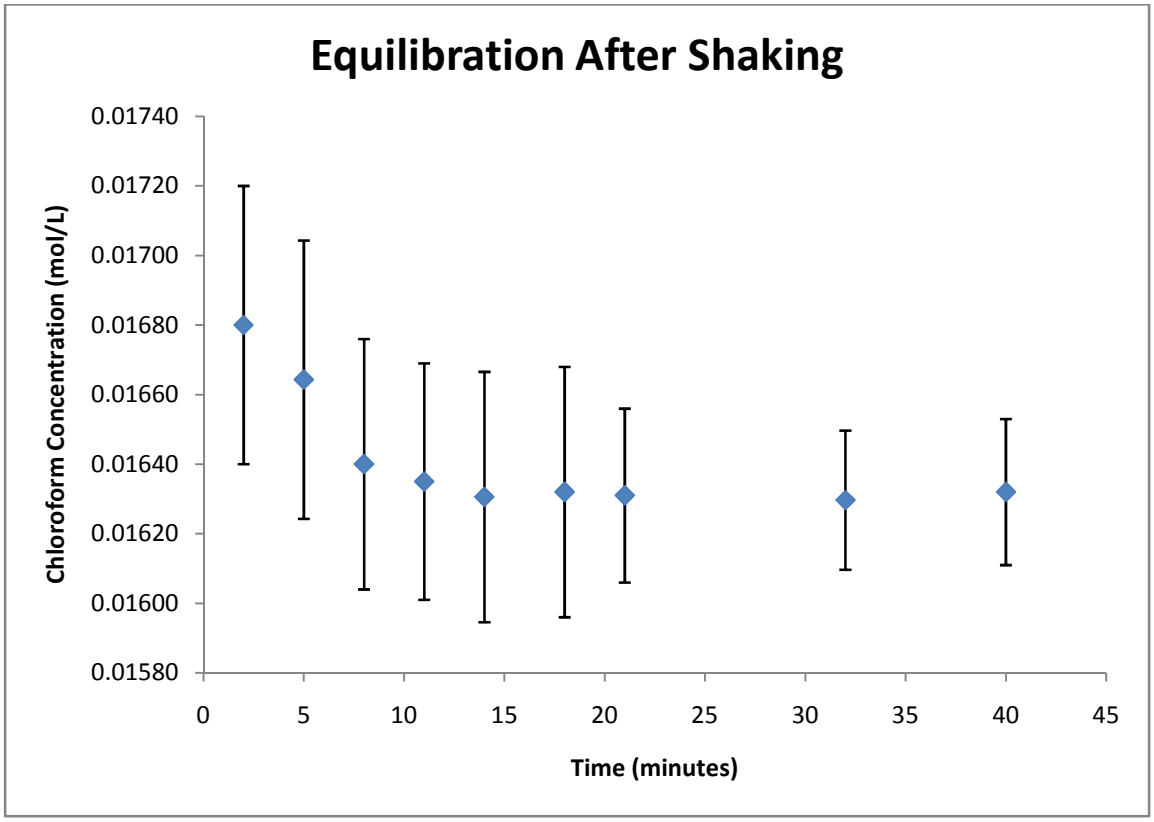


**Figure 8. Equilibration after shaking. Sample of 0.0079 M chloroform and 0.016 M dichloromethane in water.**

Based on the data, a relaxation time of 30 minutes ± 5 minutes relaxation was chosen for this testing, which allows enough time for the droplets to coalesce.

## 2.6 Buffer Selection

Since the goal of this test is to study the kinetics of this reaction at different pH values, a buffer must be identified that will allow the reaction to be run without a change in pH even as acidic or basic products are formed. The buffer must also not interfere with the reaction. In this case, a non-interfering buffer means that the buffer cannot react with hydroxyl radicals, chloroform, or absorb UV light.

Phosphate is an attractive buffer for a variety of reasons. It is triprotic, which means that a single anion acts as a buffer across a wide range of pH values. Another

attractive aspect of phosphate as a buffer is that it does not absorb a significant amount of light from a mercury lamp, 253 nm as shown in Figure 9, and it is not decomposed by hydroxyl radical.

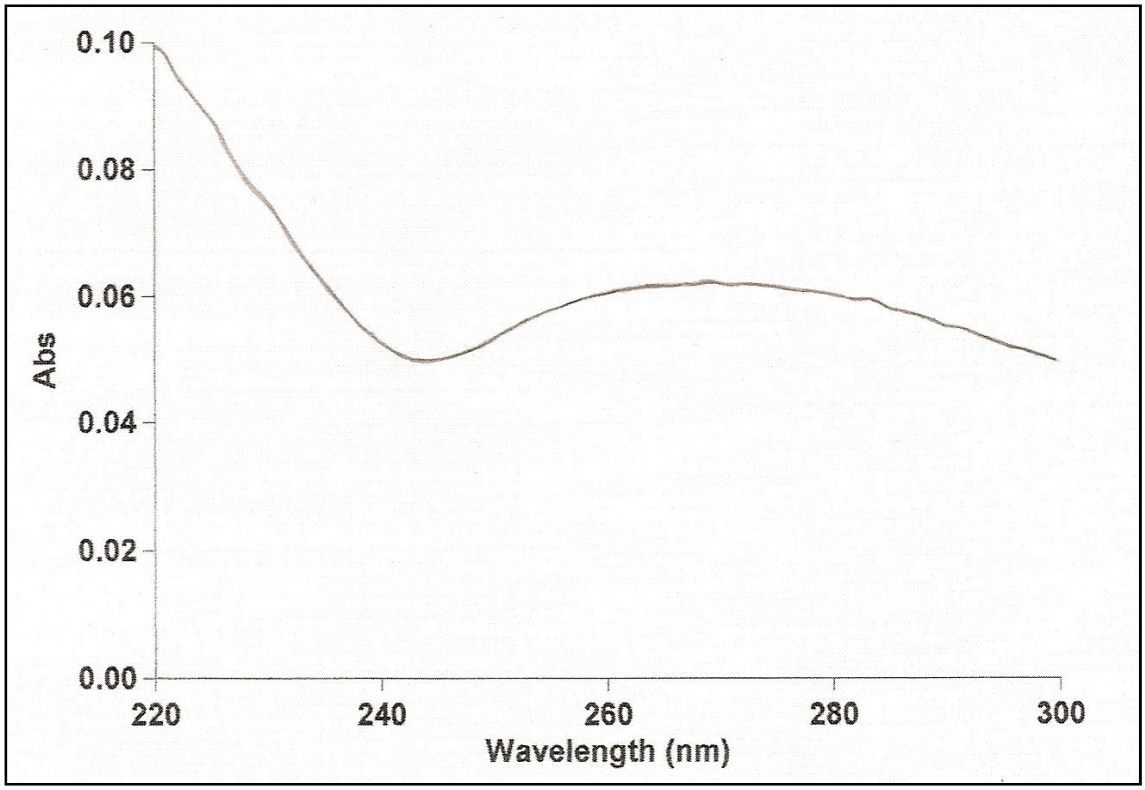


**Figure 9. UV-VIS spectrum of phosphate in water. Conditions: 1.00 M sodium phosphate buffer at pH 7.**

2.7 Comprehensive Experimental Method

To prepare samples for UV irradiation, A 1.00 M sodium phosphate buffer of the appropriate pH is prepared by titration of stock $NaH_2PO_4$ solution with $H_3PO_4$ or NaOH. 12.1 mL buffer is added to a 50 mL beaker. 0.867 mL 30% hydrogen peroxide solution is added to the buffer followed by 13.0 mL saturated chloroform water solution and the mixture stirred with a glass rod until the mixture is visually homogenous (about 5

seconds). The solution is immediately covered with parafilm to minimize loss of the volatile chloroform.

2.00 mL of the solution is pipetted into each of (6) 10 mL quartz test tubes. Immediately after solution is added to a tube, it is capped with a septum to minimize loss of chloroform. A 27 gauge, 12 mm needle is placed through each septum so that production of oxygen during the decomposition of hydrogen peroxide does not cause pressure buildup.

The six quartz test tubes are placed in a UV irradiation box (Figure 10), equidistant from the light, in a test tube rack that does not block the light path. The samples are placed 6 inches from the light (Breathe Easy 18 watt, UVC low pressure mercury vapor). The box is cross-ventilated with a box fan for flow across the samples to prevent the temperature from rising during irradiation. A dummy test tube equipped with a thermocouple is placed in the test tube rack with the other samples and temperature is monitored over the course of the experiment.

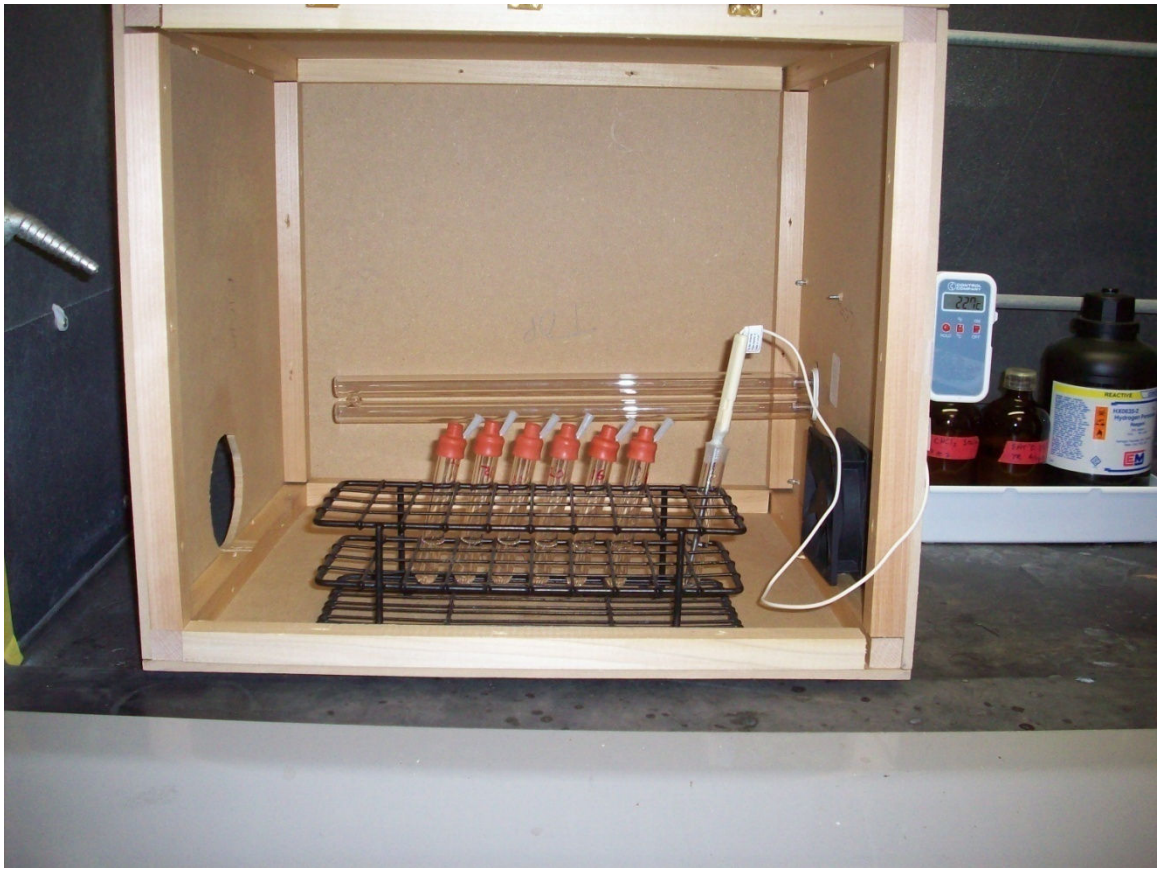

**Figure 10. UV irradiation box.**

Two milliliters solution is added to a standard Pyrex 10 mL test tube which is also capped with a septum immediately. 0.170 mL saturated dichloromethane-water solution is added to the test tube and then it is re-capped with the septum. The tube is shaken vigorously to mix the two solutions and then placed into a test tube rack to settle for 30 minutes. A 27 gauge, 12 mm needle is placed through the septum to avoid buildup of pressure due to decomposition of hydrogen peroxide.

At 10 min, 20 min, 30 min, 60 min, 90 min, and 120 min, one quartz tube is removed from the irradiation chamber. An aliquot of 0.170 mL saturated dichloromethane-water solution is added to each tube and they are shaken and allowed to settle for 30 minutes as described above.

Thirty minutes from the time each tube is shaken, 10 μL gas is removed from the headspace through the septum and analyzed with a Fisons GC8060 gas chromatograph equipped with a Hewlett Packard model 19091J-413 30 m x 0.32 mm column. The gas chromatograph is coupled to a Fisons TRIO1000 quadrupole mass spectrometer with electron impact (EI) ionization. Helium is used as a carrier gas, with a flow pressure of 5 psi. The GC routine is set to 230 °C inlet temperature, 50 °C isothermal oven temperature, 2 minutes duration.

Data is collected by monitoring mass 83 and 85 peak intensity relative to the mass 86 intensity to produce an internal concentration at the specified time. Concentration of chloroform is plotted as a function of time so that the data can be subjected to further analysis. Raw data is given in Appendix I.

# CHAPTER 3. EXPERIMENTAL ANALYSIS

The initial hypothesis was that the decomposition of chloroform was slowed or stopped at high pH. One researcher hypothesized that a competing reaction removed hydrogen peroxide by decomposition with hydroxide ions.[11] Sodium percarbonate solutions have been found to have a pH of about 12, so the purpose of this study was to further investigate the reaction kinetics of decomposition of chloroform as a function of pH.

For the experiments performed, chloroform concentration was chosen to be in the linear dynamic range of the GC-MS calibration curve in Figure 7. Based on the calibration curve data, nominal concentration was chosen to be 0.0079 M.

Initially, a hydrogen peroxide concentration of 0.12 M was arbitrarily chosen. As shown in Figure 11, it is difficult to tell whether the chloroform decomposition follows a linear trend or an exponential trend.

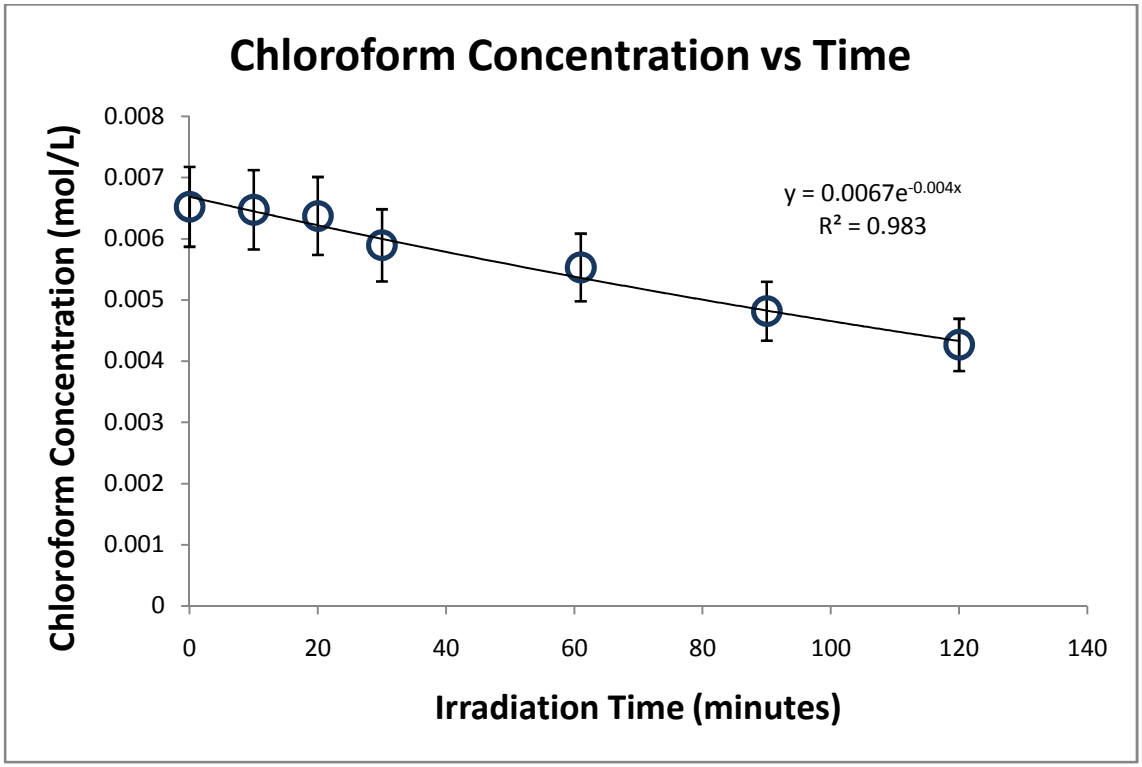


**Figure 11. Chloroform concentration vs. time. Conditions: 0.12 M H2O2 and 0.0079 M chloroform.**

In an attempt to more clearly show whether the chloroform decay was linear or exponential, the hydrogen peroxide concentration was doubled. As can be seen below in Figure 12, the decomposition of chloroform is more clearly exponential. Because of this, 0.24 M was chosen as a minimum concentration of hydrogen peroxide and that concentration was doubled and quadrupled to obtain the range used in this testing.

Several solutions, shown below in Table 6, were evaluated to establish a baseline set of data for the decomposition of chloroform under varying pH, varying hydrogen peroxide concentration, and varying chloroform concentration. A nominal pH of 7 was chosen so that data could be collected at both higher and lower pHs for comparison.

**Table 6. List of experiments for baseline data set**

| Experiment Number | pH | Chloroform Concentration (mol/L) | Hydrogen Peroxide Concentration |
|---|---|---|---|
| 1 | 7 | 0.0079 | 0.48 |
| 2 | 7 | 0.0079 | 0.24 |
| 3 | 7 | 0.0079 | 0.96 |
| 4 | 7 | 0.0039 | 0.48 |
| 5 | 7 | 0.0158 | 0.48 |
| 6 | 12 | 0.0079 | 0.48 |
| 7 | 2 | 0.0079 | 0.48 |

Table 6 describes three categories of experiments. In experiments 2 and 3, the concentration of hydrogen peroxide was varied, in experiments 4 and 5, the concentration of chloroform was varied, and in experiments 6 and 7, the pH was varied. Experiment 1 concentrations are considered "nominal" for this set of experiments and these data are included in each category of experiment.

All seven experiments were performed with the method previously described in section 2.7. A typical plot of the data collected is shown in Figure 12 (below). Conditions for the data shown in Figure 12 correspond to Experiment 1 in Table 6.

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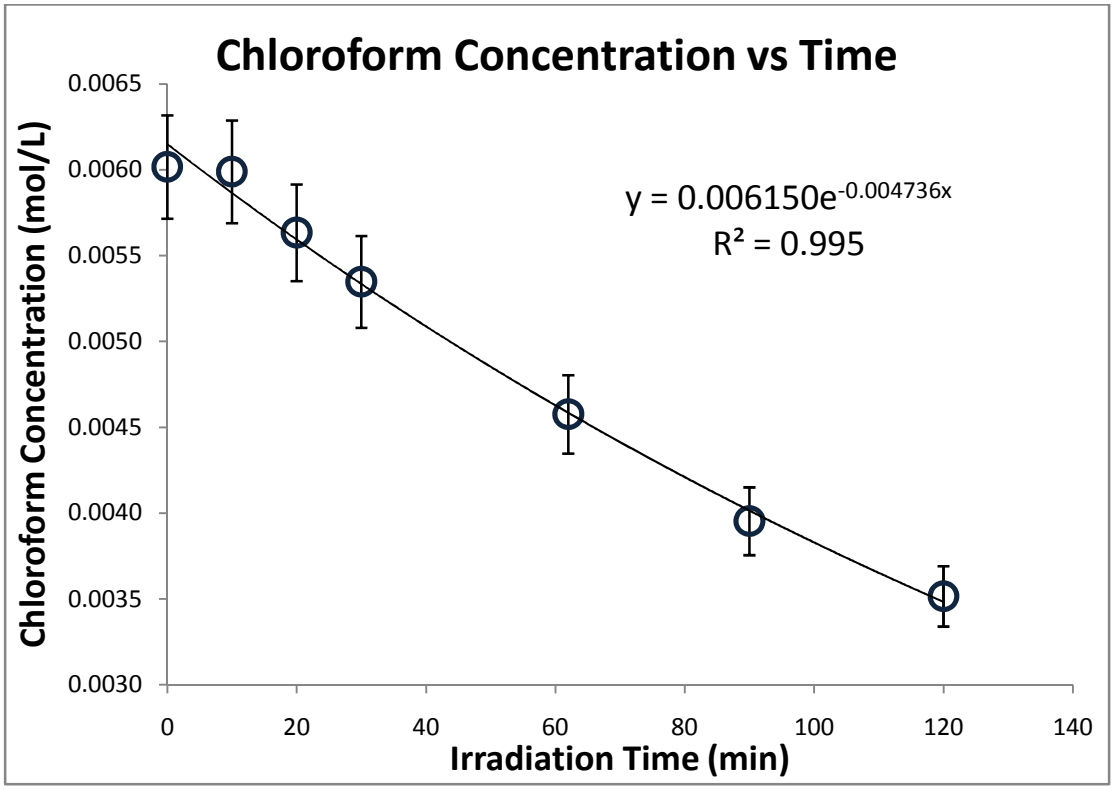


**Figure 12. Chloroform concentration vs. time. Conditions: 0.0079 M chloroform, 0.48 M hydrogen peroxide.**

Uncertainties in the data are determined from the calibration curve shown in Figure 7. Discordant points were sometimes removed if the deviation from the fitted curve exceeded the experimental uncertainty. An example of a discordant point can be found in Figure C, Appendix II. The deviation of the sixty minute sample was found to exceed experimental uncertainty, so the data was excluded from regression analysis.

As mentioned above, the data suggests an exponential decay which can be explained by first order kinetics of decomposition. A simple effective mechanism, consistent with the observed first order decay kinetics, can be written:

$$CHCl_3 + \cdot OH \overset{k_1}{\rightarrow} I \qquad (4a)$$

$$I \xrightarrow{k_2} Products + \cdot OH \tag{4b}$$

In the first step, chloroform reacts with a hydroxyl radical to form an "intermediate." This intermediate may represent several fast steps. As long as the subsequent steps are sufficiently fast, the rate constant of the first reaction will dictate the overall reaction rate. This is demonstrated later in Equations 13 through 28.

In the second step, the intermediate decomposes into products and reproduces a hydroxyl radical, which therefore acts as a catalyst. Products were not identified or measured in this study.

Time derivatives for the concentration of each species are shown below:

$$\frac{d[CHCl_3]}{dt} = -k_1[CHCl_3][\cdot OH] \tag{5a}$$

$$\frac{d[I]}{dt} = k_1[CHCl_3][\cdot OH] - k_2[I] \tag{5b}$$

$$\frac{d[P]}{dt} = k_2[I] \tag{5c}$$

$$\frac{d[\cdot OH]}{dt} = -k_1[CHCl_3][\cdot OH] + k_2[I] \tag{5d}$$

The chloroform rate law (5a), second order overall, is first order in both chloroform concentration and hydroxyl radical concentration.

In the following analysis we make the ad-hoc assumption that the intermediate (I) builds in concentration at a rate determined by reaction 4a and then is consumed at an identical rate determined by reaction 4b. In this case the net concentration change is zero and a steady state approximation can be applied. The concentration of the intermediate must remain low in order to apply the steady state approximation.

$$\frac{d[I]}{dt} = 0 \tag{6}$$

Setting 5b equal to zero yields

$$k_1[CHCl_3][\cdot OH] - k_2 = 0 \tag{7}$$

And thus

$$\frac{k_1}{k_2}[CHCl_3][\cdot OH] = [I] \tag{8}$$

Re-arranging:

$$-k_1[CHCl_3][\cdot OH] + k_2[I] = 0 = -\frac{d[I]}{dt} \tag{9}$$

Substitution into 5d gives

$$\frac{d[\cdot OH]}{dt} = 0 \tag{10}$$

If the steady-state assumption made above is correct, then this suggests a steady state concentration for hydroxyl radicals. If the hydroxyl radical concentration is constant, the equation can be represented as shown below, where constant concentration of hydroxyl radicals is combined with the rate constant.

$$\frac{d[CHCl_3]}{dt} = -k'[CHCl_3] \tag{11}$$

Integration yields the following equation, which shows exponential decay of chloroform concentration.

$$[CHCl_3] = [CHCl_3]_0 e^{-k't} \tag{12}$$

This can be used to fit the collected data and to determine an effective constant (k').

In the event that more than one intermediate is produced, as long as the reaction rates are fast, the effective rate constant, k' is not affected. An example is shown below, where the overall chemical reaction is the same but with an additional intermediate.

$$CHCl_3 + \cdot OH \overset{k_1}{\rightarrow} I_1 \tag{13}$$

$$I_1 \overset{k_2}{\rightarrow} I_2 \tag{14}$$

$$I_2 \overset{k_3}{\rightarrow} Products + \cdot OH \tag{15}$$

The time derivatives for the concentration of each species are:

$$\frac{d[CHCl_3]}{dt} = -k_1[CHCl_3][\cdot OH] \tag{16}$$

$$\frac{d[I_1]}{dt} = k_1[CHCl_3][\cdot OH] - k_2[I_1] \tag{17}$$

$$\frac{d[I_2]}{dt} = k_2[I_1] - k_3[I_2] \tag{18}$$

$$\frac{d[P]}{dt} = k_3[I_2] \tag{19}$$

$$\frac{d[OH]}{dt} = -k_1[CHCl_3][\cdot OH] + k_3[I_2] \tag{20}$$

Once again, it is assumed that since the intermediates are produced in one step and consumed at the same rate in another step, the concentration is constant, as shown in Equations 21 and 22.

$$\frac{d[I_1]}{dt} = 0 \tag{21}$$

$$\frac{d[I_2]}{dt} = 0 \tag{22}$$

Setting Equations 17 and 18 equal to zero

$$k_1[CHCl_3][\cdot OH] - k_2[I_1] = 0 \quad (23)$$

$$k_2[I_1] - k_3[I_2] = 0 \quad (24)$$

Rearranging

$$[I_1] = \frac{k_1}{k_2}[CHCl_3][\cdot OH] \quad (25)$$

$$[I_2] = \frac{k_2}{k_3}[I_1] \quad (26)$$

Substitution gives

$$[I_2] = \frac{k_1}{k_3}[CHCl_3][\cdot OH] \quad (27)$$

Combination with Equation 19 gives

$$\frac{d[P]}{dt} = k_1[CHCl_3][\cdot OH] \quad (28)$$

This shows that the rate of appearance of products is independent of the concentration of both intermediates.

Assuming that the kinetics follow exponential decay, as shown in Equation 12, data for each of the seven experiments in Table 6 were fit to exponential regression. Plots for all experiments are attached in Appendix A. Once the rate constants for each experiment were determined, their dependence on chloroform concentration, hydrogen peroxide concentration, and pH were all examined. The rate constant k' was plotted as a function of pH, hydrogen peroxide concentration, and chloroform concentration as shown in Figures 13 – 15. In all of the figures below, the error bars were obtained by running three replicate samples at nominal concentrations and then determining the standard deviation of the fit. Similar uncertainties in rate constant were assumed for all runs.

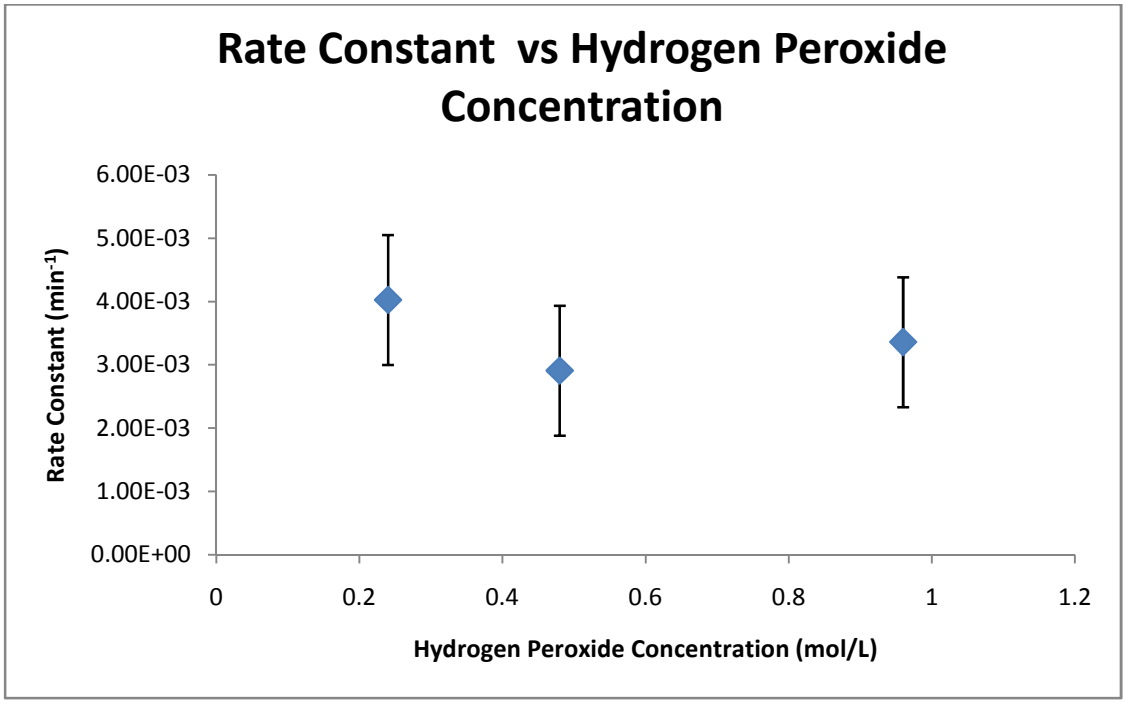


**Figure 13. Rate constant vs. hydrogen peroxide concentration. Conditions: 0.0079 M chloroform, pH 7, 0.24 M, 0.48 M, 0.96 M hydrogen peroxide.**

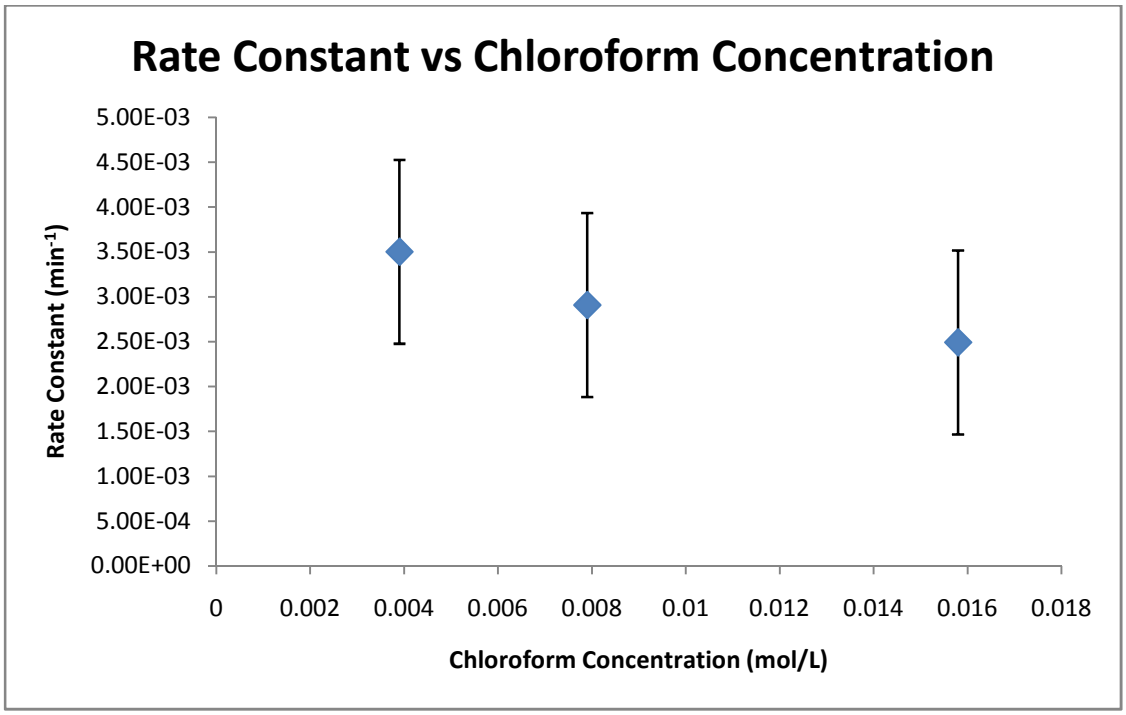


**Figure 14. Rate constant vs. chloroform concentration. Conditions: 0.48 M hydrogen peroxide, pH 7, 0.0039 M, 0.0079 M, 0.0158 M chloroform.**

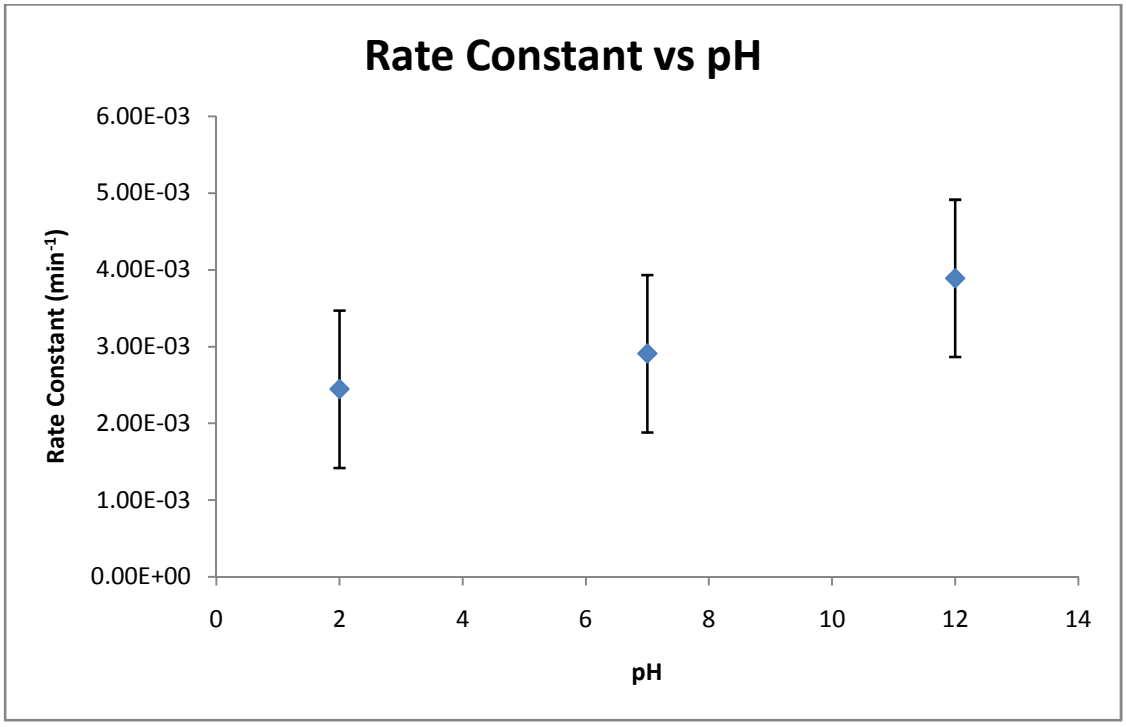


**Figure 15. Rate constant vs. pH. Contitions: 0.0079 M chloroform, 0.48 M hydrogen peroxide, pH 2, 7, and 12.**

As is seen in Figures 13 through 15, within experimental uncertainty there is no discernable dependence of k' on hydrogen peroxide concentration, chloroform concentration, or pH. There may actually be a dependence on pH but the large error makes this determination difficult with the current data. Any conclusions about the dependence of k' on chloroform or hydrogen peroxide concentration would require a substantially reduced experimental uncertainty.

This is not conclusive, but with experimental uncertainty, is consistent with the data gathered in this study. The fact that there is no dependence of pH on the kinetics is contrary to the original hypothesis that the reaction slowed or shut off at high pH, as observed by Rudra et al.[11] (86% removal of chloroform in 75 minutes at pH 2.5 but only75% removal of chloroform in 90 minutes at pH 10).

Rudra et al. suggested a competing reaction for hydrogen peroxide at high pH.[11]

$$H_2O_2 + OH^- \rightarrow \cdot OOH + H_2O \quad (13)$$

It was noted that Rudra et al. used significantly lower concentrations of chloroform and hydrogen peroxide (1.69 μM chloroform and 0.029 M hydrogen peroxide). The fact that the hydrogen peroxide concentration was an order of magnitude lower and the chloroform concentration was several orders of magnitude lower than the concentration used in this study may help explain the discrepancy in findings.

At the high relative concentration of hydrogen peroxide to chloroform used in this series of experiments, the competing reaction suggested by Rudra et al. may not be significant enough to affect the decomposition of chloroform. It is also possible that ·OOH may initiate decomposition via a different mechanism. In light of this data, sodium percarbonate solutions were re-visited.

It is possible that the high concentration of hydrogen peroxide swamps any competing reactions which may affect overall observed decomposition of chloroform reported by Rudra et al.. Therefore, a sodium percarbonate solution was prepared as in previous studies for a baseline (0.20 M hydrogen peroxide, pH 12) and another sodium percarbonate solution was prepared and then spiked with hydrogen peroxide up to concentrations (0.48 M hydrogen peroxide, pH 12) used in the nominal experiment. It was found that the sodium percarbonate solution that was spiked with hydrogen peroxide showed a similar rate constant as the high pH phosphate solution but the baseline SPC only solution showed a markedly reduced rate constant, as shown in Figure 16.

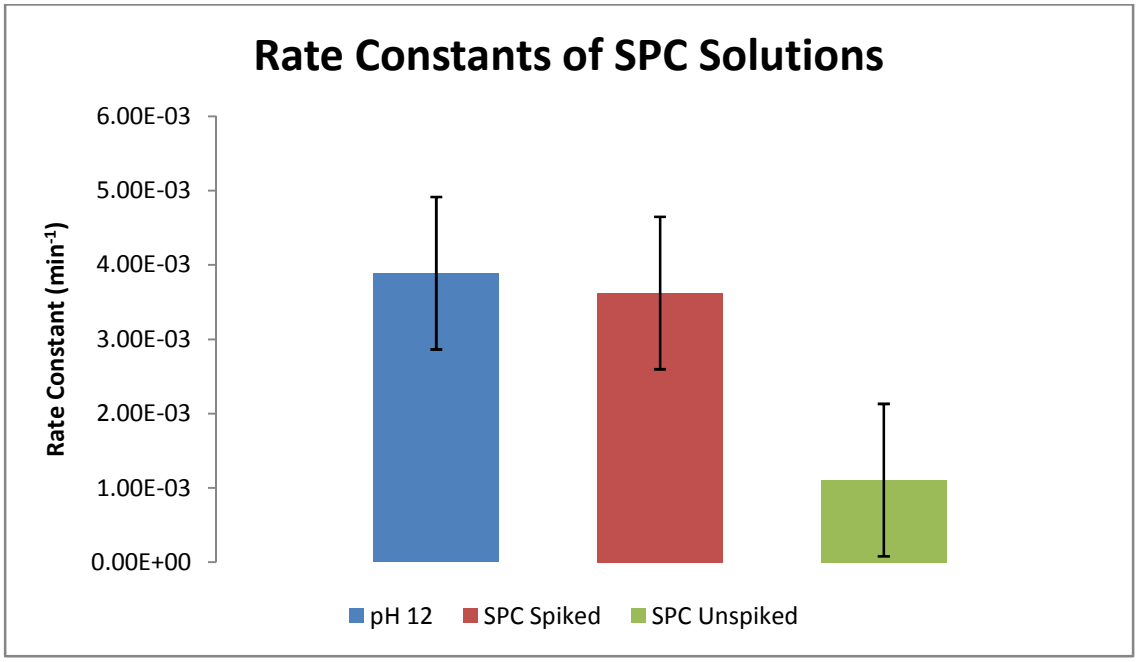


**Figure 16. Rate constants of SPC solutions. From left: 0.0079 M chloroform, 0.48 M hydrogen peroxide, pH 12 sodium phosphate buffer; 0.0079 M chloroform, 0.48 M hydrogen peroxide, pH 12 sodium percarbonate solution; 0.0079 M chloroform, 0.20 M hydrogen peroxide, pH 12 sodium percarbonate solution.**

As can be seen in Figure 16, when a solution with a lower concentration of hydrogen peroxide was tested, a reduced rate constant was observed. Figures 17 and 18 show the rate constant dependence on hydrogen peroxide concentration at pH 7 and pH 12.

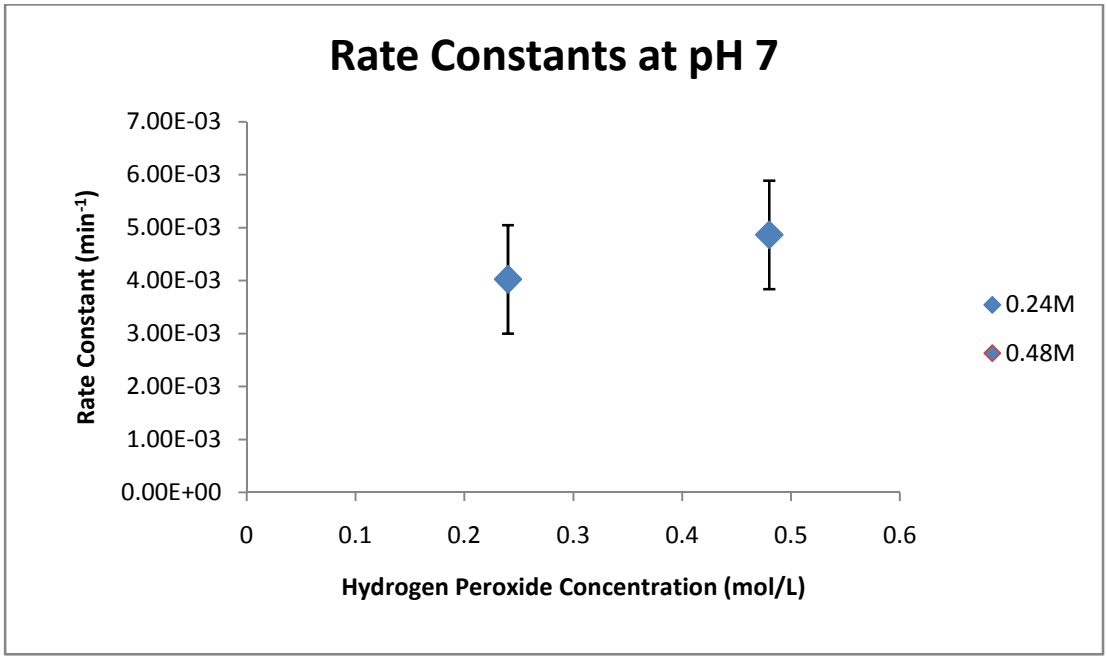


**Figure 17. Rate Constants at pH 7. Conditions: 0.0079 M chloroform, 120 min irradiation.**

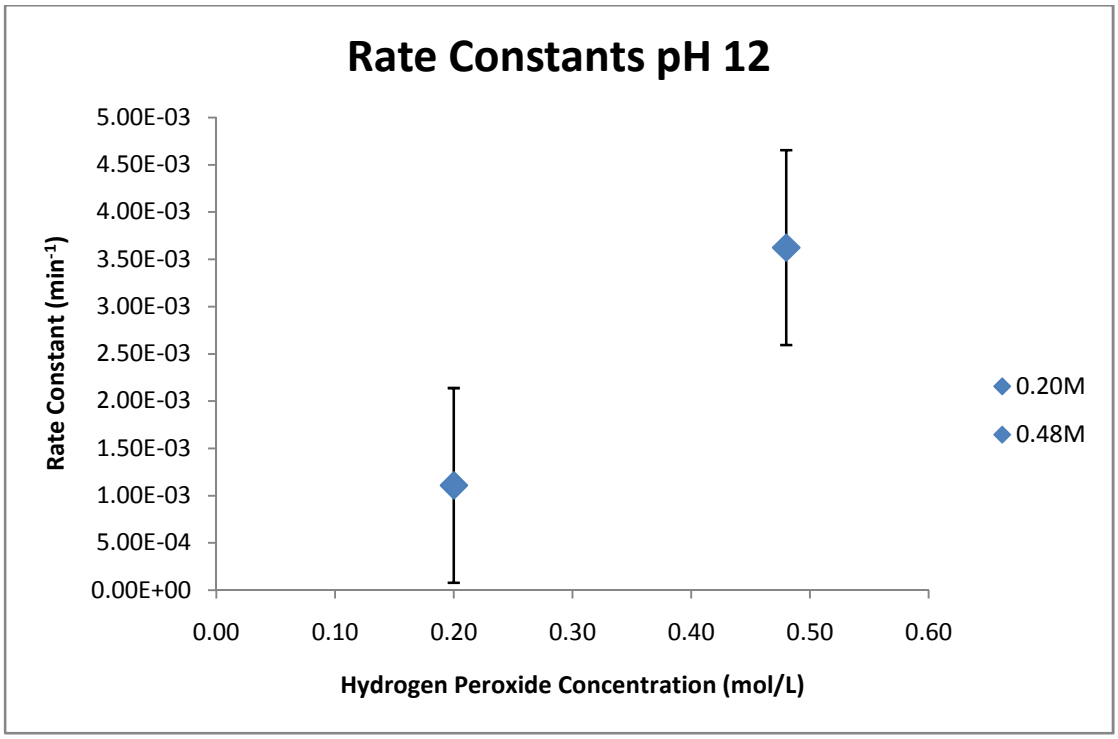


**Figure 18. Rate constants at pH 12. Conditions: 0.0079 M chloroform, 120 min irradiation.**

It is clear from the plots that under these conditions, there is a dependence of hydrogen peroxide concentration on the rate constant at pH 12 but not at pH 7. The observations in the high pH case agree with Rudra et al.'s observations.[11] It is interesting to note that the difference in rate constant is undetectable between pH 7 and pH 12 at 0.48M hydrogen peroxide, but clear between pH 7 and pH 12 at 0.20 M hydrogen peroxide, as shown in Figures 19 and 20.

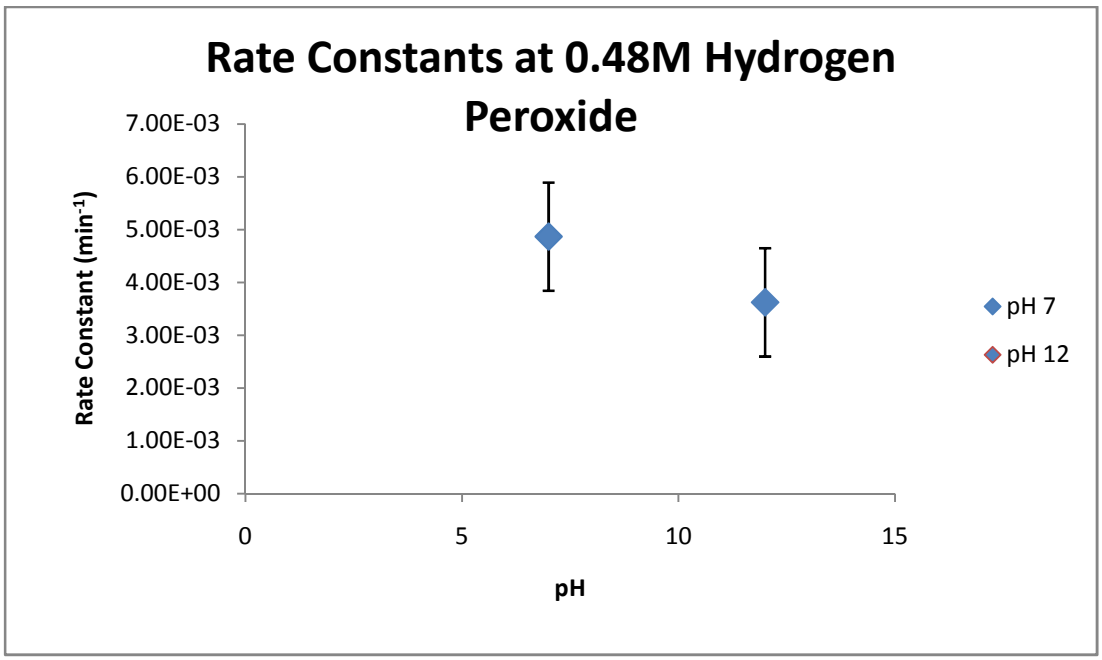


**Figure 19. Rate constants at 0.48 M hydrogen peroxide**

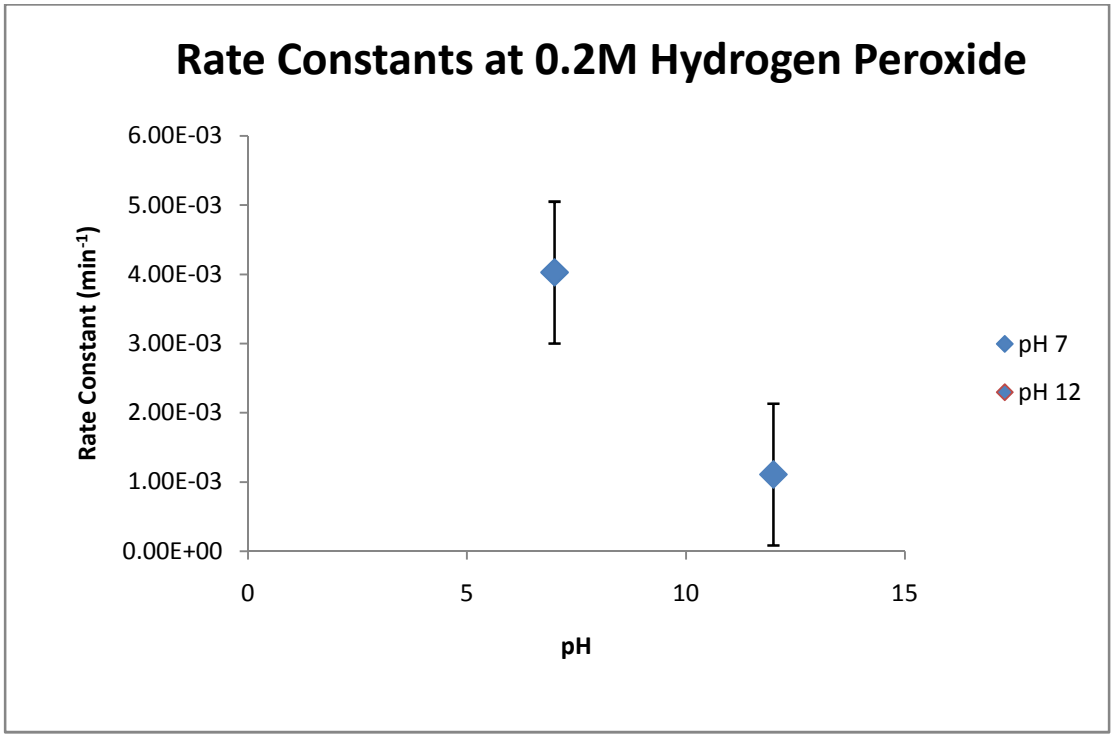


**Figure 20. Rate constants at 0.2 M hydrogen peroxide**

This data further supports the hypothesis that a competing reaction removes hydroxyl radicals at high pH. It suggests that a competing reaction that affects the rate constant at pH 12 is swamped above a certain concentration of hydrogen peroxide.

# CHAPTER 4. CONCLUSIONS AND FUTURE WORK

A quantitative analytical method for the determination of concentration of chloroform in water by GCMS has been developed. This method makes use of the volatility of chloroform by sampling from headspace instead of a traditional time consuming liquid extraction, and uses a common and easy to obtain chemical, dichloromethane, as internal standard. Finally, this method requires no specialized or expensive additional equipment beyond the GC-MS instrument.

The data in this study suggests that under the conditions tested (0.0039 M to 0.058 M chloroform, 0.24 M to 0.96 M hydrogen peroxide at pH 7, and 0.0079 M chloroform and 0.48 M hydrogen peroxide at pH 2, pH 7, and pH 12), the proposed rate constant k' is independent of chloroform concentration and pH. A dependence of rate constant on hydrogen peroxide concentration between 0.20 M and 0.48 M at pH 12 was found. These altered kinetics could be due to a competing reaction at pH 12.

Two important assumptions made in this study were the catalytic nature and resultant steady state concentration of the hydroxyl radical, but the concentration of hydroxyl radical was not directly measured. In order to verify the conclusions made about this chemistry, the hydroxyl radical concentration as a function of time should be measured. Study of the concentration of a radical can be done by electron paramagnetic resonance (EPR), where unpaired electrons are measured as they interact with an electromagnetic field. A more thorough understanding of the concentration of hydroxyl

radical as a function of time is essential to gaining a complete picture of this chemistry as this will help elucidate the participatory role it plays.

Another useful experiment would be to study the concentration of hydrogen peroxide as a function of time in high pH SPC solutions. At low concentrations of hydrogen peroxide, the decomposition of hydrogen peroxide by hydroxide ions might be significant enough to affect the kinetics of decomposition of chloroform by hydroxyl radical. This would be significant because as shown above, sodium percarbonate solutions release relatively low concentrations of hydrogen peroxide (about 0.20 M), and the decomposition of chloroform might be slowed significantly or stopped completely.

Finally, chloroform can be effectively decomposed using hydrogen peroxide/UV as a decomposition reagent system across the complete range of pH examined in this study, provided the hydrogen peroxide concentration is sufficiently large.

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## APPENDIX I. RAW DATA

Below is a table of raw data for the seven experiments. Values are in mol/L chloroform.

**Table A. Experimental conditions.**

| Experiment Number | pH | Chloroform Concentration (mol/L) | Hydrogen Peroxide Concentration |
|---|---|---|---|
| 1 | 7 | 0.0079 | 0.48 |
| 2 | 7 | 0.0079 | 0.24 |
| 3 | 7 | 0.0079 | 0.96 |
| 4 | 7 | 0.0039 | 0.48 |
| 5 | 7 | 0.0158 | 0.48 |
| 6 | 12 | 0.0079 | 0.48 |
| 7 | 2 | 0.0079 | 0.48 |
| SPC Unspiked | 12 | 0.0079 | 0.48 |
| SPC Spiked | 12 | 0.0079 | 0.20 |

**Table B. Raw data**

| | Timepoint | | | | | | |
|---|---|---|---|---|---|---|---|
| Experiment # | 0 min | 10 min | 20 min | 30 min | 60 min | 90 min | 120 min |
| 1 | 6.0E-03 | 6.0E-03 | 5.6E-03 | 5.3E-03 | 4.6E-03 | 4.0E-03 | 3.5E-03 |
| Repeat 1 | 4.6E-03 | 4.7E-03 | 4.8E-03 | 5.0E-03 | 4.3E-03 | 4.0E-03 | 3.5E-03 |
| Repeat 2 | 5.3E-03 | 5.1E-03 | 4.5E-03 | 4.6E-03 | 3.9E-03 | 3.9E-03 | 3.5E-03 |
| 2 | 5.1E-03 | 4.9E-03 | 4.8E-03 | 4.3E-03 | 3.9E-03 | 3.5E-03 | 3.2E-03 |
| 3 | 5.4E-03 | 5.3E-03 | 5.2E-03 | 4.8E-03 | 4.0E-03 | 3.9E-03 | 3.7E-03 |
| 4 | 2.4E-03 | 2.4E-03 | 2.6E-03 | 2.1E-03 | 2.1E-03 | 1.8E-03 | 1.6E-03 |
| 5 | 1.3E-02 | 1.1E-02 | 1.1E-02 | 1.1E-02 | 9.9E-03 | 9.7E-03 | 8.2E-03 |
| 6 | 6.2E-03 | 5.7E-03 | 5.6E-03 | 5.4E-03 | 4.7E-03 | 4.1E-03 | 3.8E-03 |
| 7 | 5.3E-03 | 5.2E-03 | 5.1E-03 | 5.4E-03 | 4.4E-03 | 4.3E-03 | 3.9E-03 |
| SPC Spiked | 5.5E-03 | 5.4E-03 | 5.5E-03 | 5.2E-03 | 4.5E-03 | 4.0E-03 | 3.7E-03 |
| SPC Unspiked | 5.6E-03 | 5.5E-03 | 5.6E-03 | 5.4E-03 | 5.3E-03 | 5.0E-03 | 4.9E-03 |

APPENDIX II. CONCENTRATION VERSUS TIME PLOTS

Below are plots of concentration of chloroform versus time for all seven experimental conditions. Open circles indicate included data, and diamonds indicate data excluded by the above mentioned method.

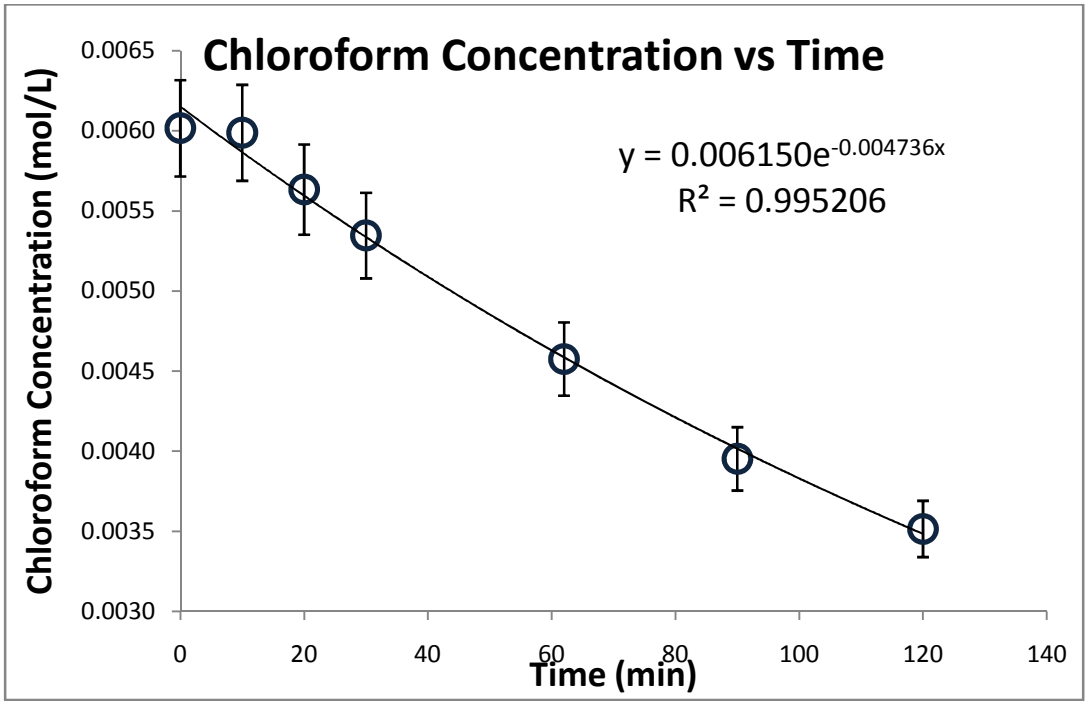


**Figure A. Nominal concentration. Conditions: 0.0079 M chloroform, 0.48 M hydrogen peroxide, pH 7 phosphate buffer.**

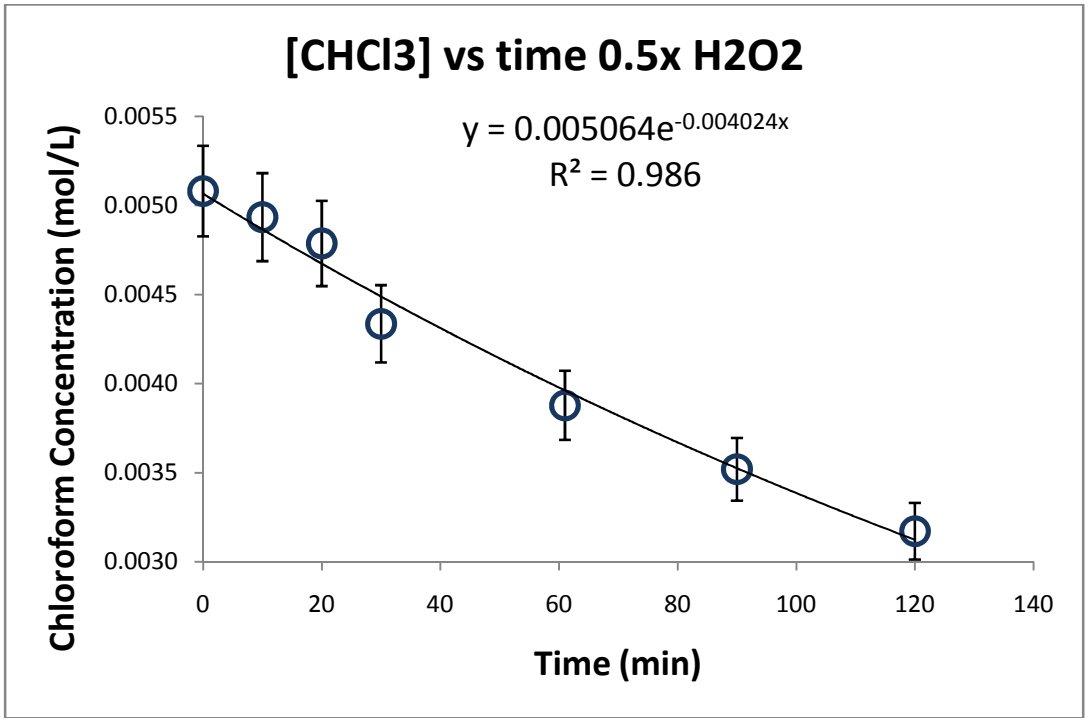


**Figure B. Half concentration hydrogen peroxide. Conditions: 0.0079 M chloroform, 0.24 M hydrogen peroxide, pH 7 phosphate buffer.**

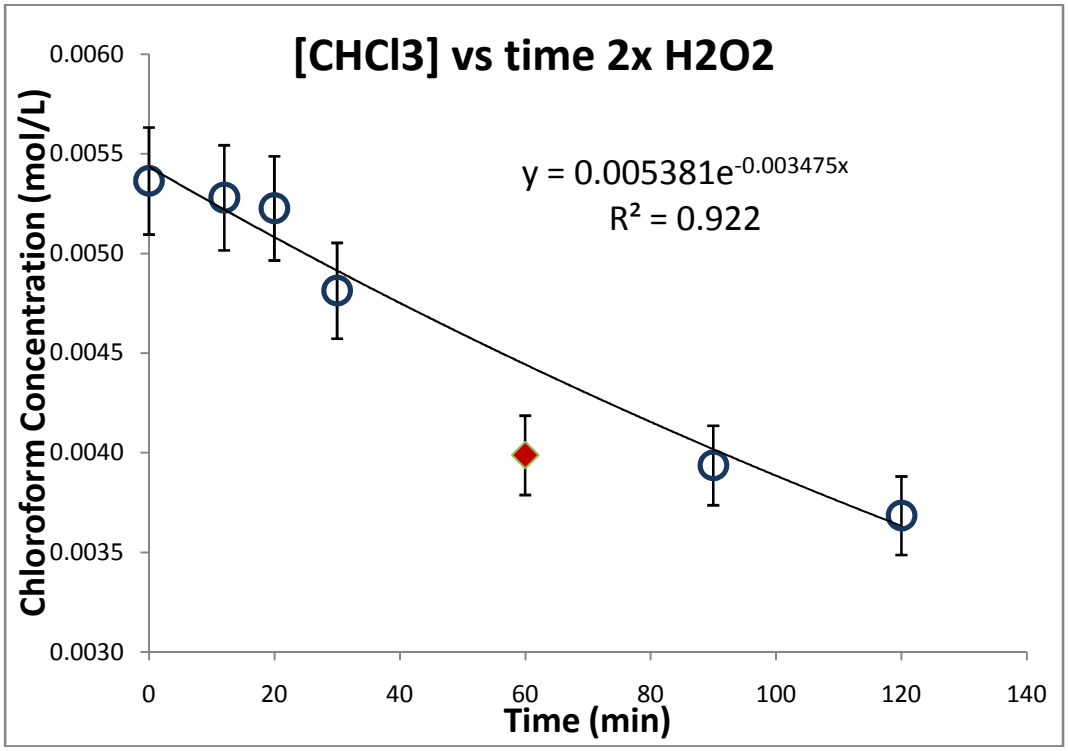


**Figure C. Double concentration hydrogen peroxide. Conditions: 0.0079 M chloroform, 0.96 M hydrogen peroxide, pH 7 phosphate buffer.**

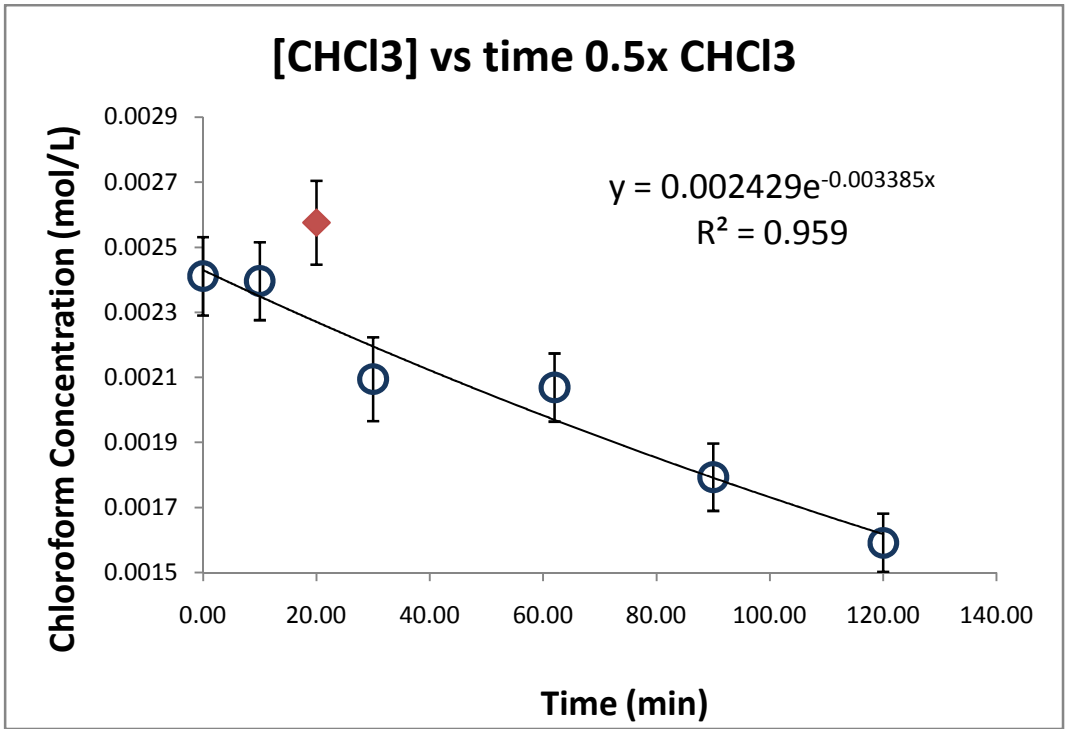


**Figure D. Half concentration chloroform. Conditions: 0.0039 M chloroform, 0.48 M hydrogen peroxide, pH 7 phosphate buffer.**

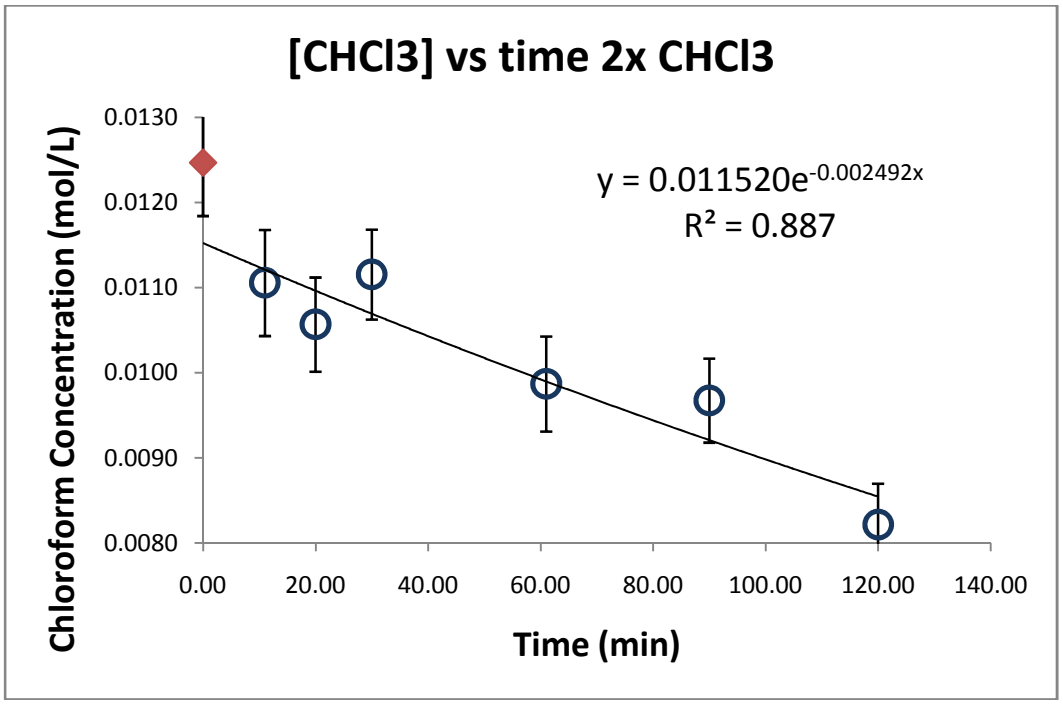


**Figure E. Double concentration chloroform. Conditions: 0.0158 M chloroform, 0.48 M hydrogen peroxide, pH 7 phosphate buffer.**

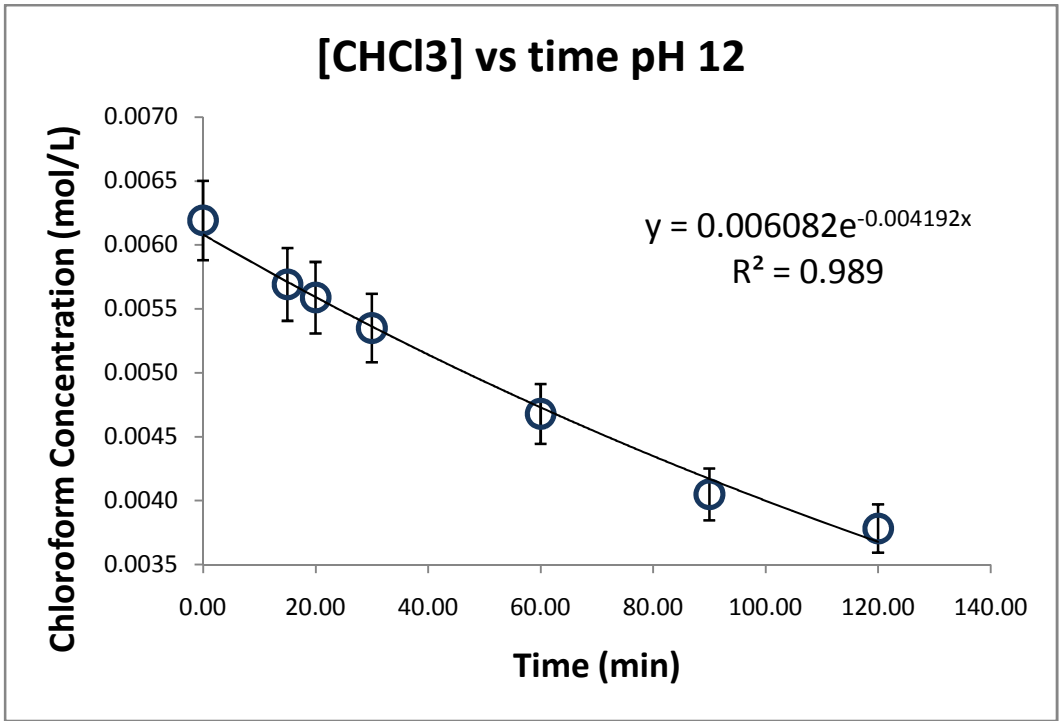


**Figure F. pH 12. Conditions: 0.0079 M chloroform, 0.48 M hydrogen peroxide, pH 12 phosphate buffer.**

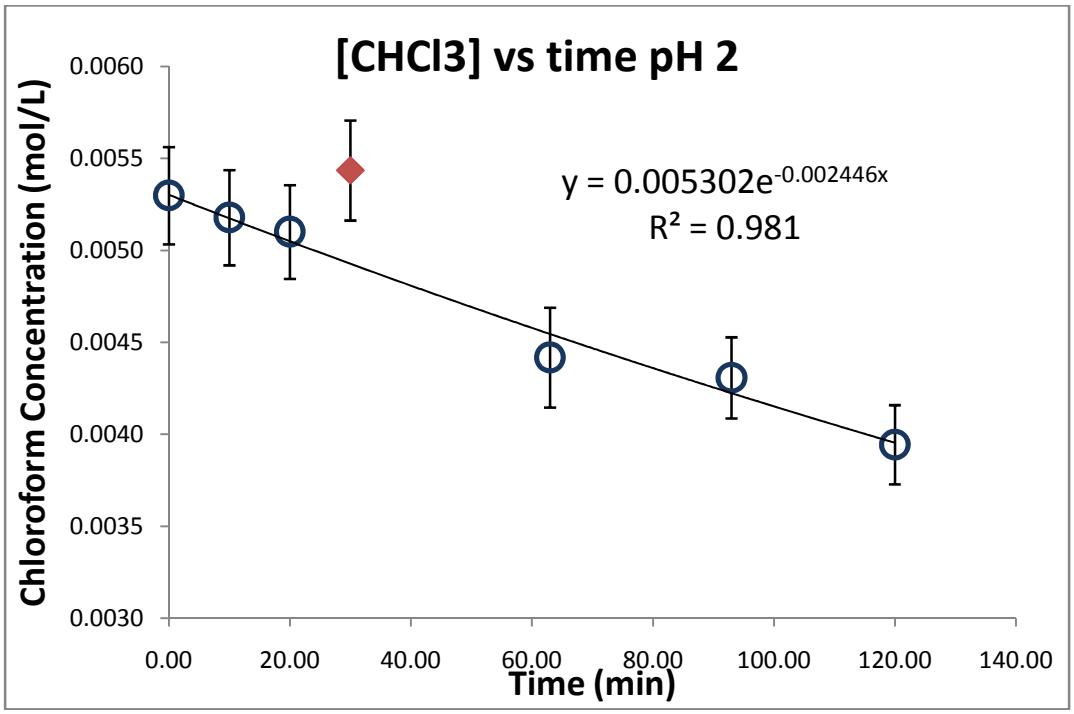


**Figure G. pH 2. Conditions: 0.0079 M chloroform, 0.48 M hydrogen peroxide, pH 2 phosphate buffer.**

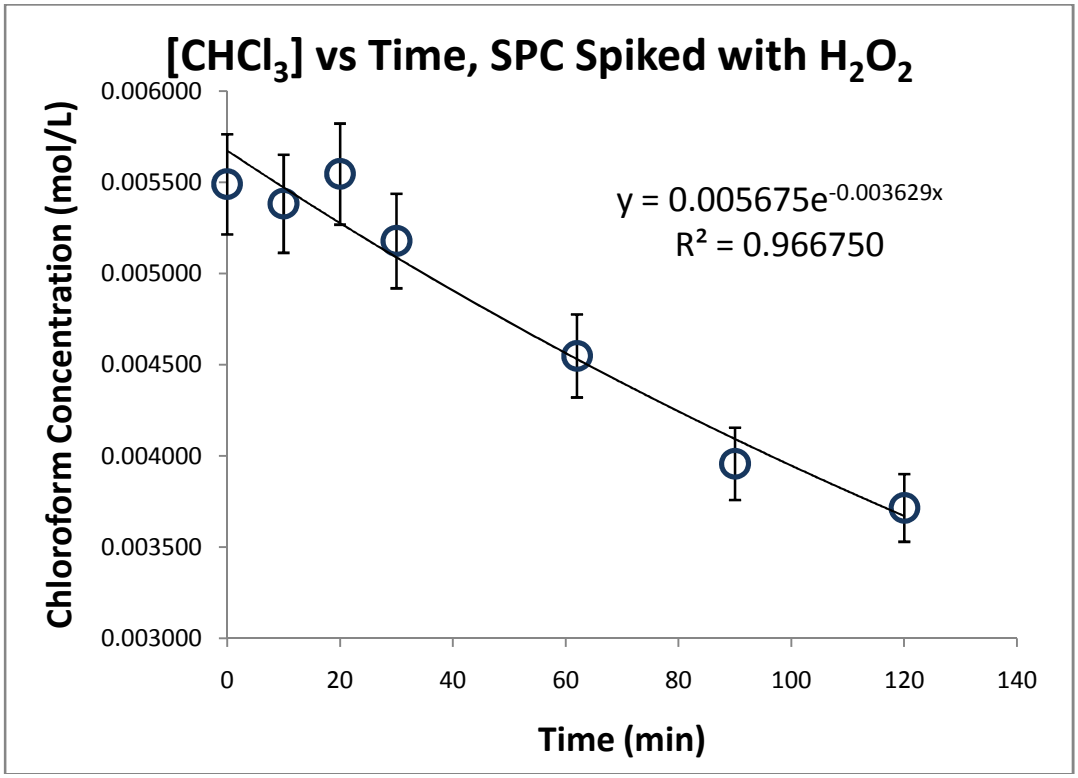


**Figure H. SPC Solution Spiked with Hydrogen Peroxide. Conditions: 0.0079 M chloroform, 0.48 M hydrogen peroxide, pH 12 sodium percarbonate solution.**

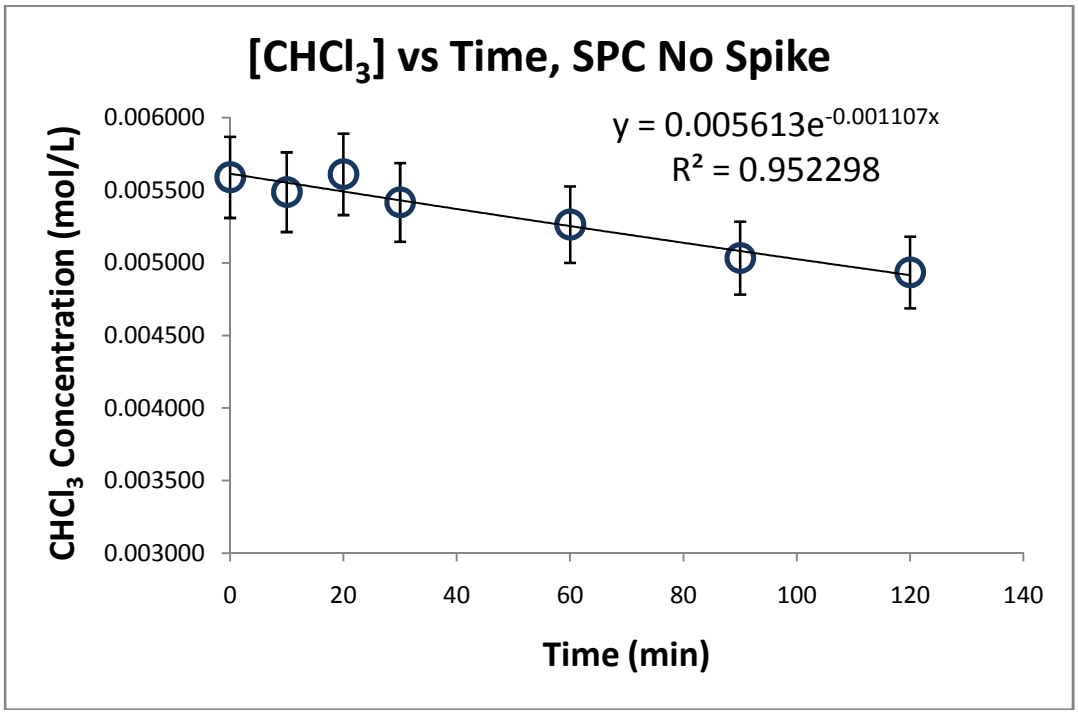


**Figure I. SPC Solution. Conditions: 0.0079 M chloroform, 0.20 M hydrogen peroxide, pH 12 sodium percarbonate solution.**